RAYLO CHEMICALS LIMITED
Subsidiary of Terochem Laboratories Limited
8045 Argyll Road, Edmonton, Alberta, Canada T6C 4A9
Telephone (403) 465-7937 Telex 037-43236

FLOCCULANTS

FINAL REPORT

By:

Raylo Chemicals Limited
8045 Argyll Road
Edmonton, Alberta
T6C 4A9

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

DSS File Number: 14SQ.23440-0-9153

DSS Contract Serial Number: OSQ80-00207

CANMET Scientific Authority: Dr. H.A. Hamza

AUG 19 1980

86pp.

MICROMEDIA

TABLE OF CONTENTS

ABSTRACT

INTRODUCTION

RESULTS AND DISCUSSION

I. Chemical Characterization of Commercial Flocculants
    1. Spectroscopic Analysis
    2. Wet Chemical Analysis
    3. Low Angle Laser Light Scattering Photometry
        a) Static Molecular Weight Determination
        b) Dynamic Molecular Weight Determination

II. Degradation of Polyacrylamides in Solution

III. Fractionation of Poyacrylamide Flocculants

CONCLUSIONS

REFERENCES

TABLES

FIGURES

RAYLO CHEMICALS LIMITED
Subsidiary of Terochem Laboratories Limited
8045 Argyll Road, Edmonton, Alberta, Canada T6C 4A9
Telephone (403) 465-7937 Telex 037-43236

ABSTRACT

A total of six commercial flocculant samples were received from Energy, Mines and Resources, and all were characterized in detail. One polyamine-based flocculant, sample 96, possessed exceptionally high molecular weight for polymers of its type. Analysis of the chloride content of cationic flocculants usually found approximately equivalent chloride and polymeric cation concentration. Three flocculants, samples 57, 64 and 77 contained added salt, whereas both sample 9 and 89 were exceptional in containing sulphate anion.

Evaluation of the reproducibility of aqueous dynamic Low Angle Laser Light Scattering (LALLS) Photometry indicated that triplicate analyses are necessary to ensure reliable results. Commercial gel permeation columns for dynamic LALLS analysis suitable for the investigation of cationic polymers were received, however tests indicated they cannot be used effectively for polymers in excess of 5 million molecular weight. Both the KMX-16 Differential Refractometer and the Digital Correlator accessory for the KMX-6 Photometer were received and are now functioning satisfactorily.

Manufacturers of Fine Chemicals & Chemical Reagents

Extensive studies of the degradation of nonionic, anionic and cationic polyacrylamides by ferrous salts and oxygen indicate the utility of chemical stabilization. Anionic polyacrylamide degradation proceeded at a substantially greater rate than that of nonionic or cationic polyacrylamide.

Synthesis of certain polyamine-based polymers termed ionenes was undertaken. Comparison of the polymerization products with polyamine flocculants investigate thus far indicates that none of the flocculant samples were ionene homopolymers. Modification of polyacrylamide-based flocculants to products soluble in organic solvents was successful, but caused substantial degradation of the polymer.

Flocculation testing carried out on samples previously fractionated at Raylo Chemicals indicated that for the system under study, an increase in polymer molecular weight above 3 million caused little increase in efficiency. A method of controlled ultrasonic degradation was developed to allow rapid and reproducible preparation of intermediate and low molecular weight derivatives of flocculants for further flocculation studies.

INTRODUCTION

This report records the work performed under the contract issued by the Department of Supply and Services (DSS File No. 14SQ.23440-0-9153) on behalf of The Department of Energy, Mines and Resources, CANMET, Western Regional Laboratory, Edmonton, Alberta. The Scientific Authority for the project was Dr. H. Hamza, head of the Western Regional Laboratory. The work was previously reported in monthly progress reports but this final report gathers all the information together and puts it in context.

BACKGROUND

The large scale introduction of coal washery techniques in Western Canada coupled with the necessity of complying with new environmental standards have necessitated development of methods for clarifying water laden with coal and coal-derived fine particulates. Since their introduction over 20 years ago, synthetic organic polymeric flocculants have attained widespread application in coal washery water clarification. In response to the demand for effective water treatment agents, a large number of commercial flocculants have been introduced, so that at present, over 100 flocculants from 30 suppliers are recommended for use in coal operations. In fact, "the user is confronted and bewildered by a host of brand names with very little technical back-up as to the nature of the flocculant and the methodology for their evaluation" (1). Difficulties also occur in maintaining satisfactory performance of the flocculants under industrial conditions due to the sensitivity of these polymers to changes in composition of the effluent water. The correlation of flocculant performance under various conditions with the chemical characteristics of the polymer would assist washery operators in choosing an appropriate product in response to detected changes in the effluent stream.

OBJECTIVE AND APPROACH

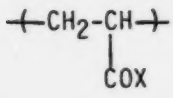
The objective of this study was ultimately to derive structure activity relationships for certain groups of polymeric flocculants and thus provide a basis for the synthesis of superior flocculating agents for specific applications. In order to meet these goals, a series of specific tasks were proposed. The chemical characterization and molecular weight analysis of flocculants including determination of their differential refractive index was continued. The examination of the solution properties of flocculants was continued, with the main emphasis being placed on the causes of and preventative measures against degradation of the macromolecules. Use of the digital correlator accessory to the Chromatix Low Angle Laser Light Scattering Photometer in the determination of particle size has begun.

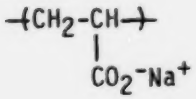
The effect of molecular weight on the coal particulate flocculating efficiency of a commercial product has been investigated in a co-operative project - Raylo fractionated the product and determined its molecular weight, while personnel of the Western Regional Laboratory of Energy, Mines and Resources carried out flocculation testing. Co-operative studies of the effects of other chemical characteristics of the polymer flocculants on performance are expected to continue in the future.

RESULTS AND DISCUSSION

I. CHEMICAL CHARACTERIZATION OF COMMERCIAL FLOCCULANTS

The development of spectroscopic and wet chemical analytical methods and the application of these methods to the chemical characterization of a large number of commercial flocculants received a great deal of effort in the earlier stages of this contract. Thus far, a total of 102 unknown flocculants supplied by the Scientific Authority and over 20 clearly identified flocculants from various sources have been investigated. The general chemical classification of the unknown flocculants is noted in Table 1. The majority of the flocculants were based on polyacrylamide, either nonionic as in structure 1, anionic





4

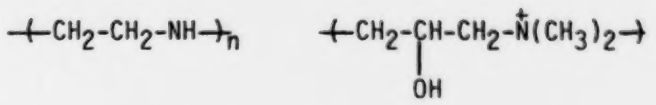
1 X = NH_2

2 X = NH_2 or O^-Na^+

3 X = NH_2 or $O\text{-}CH_2CH_2NH_2$

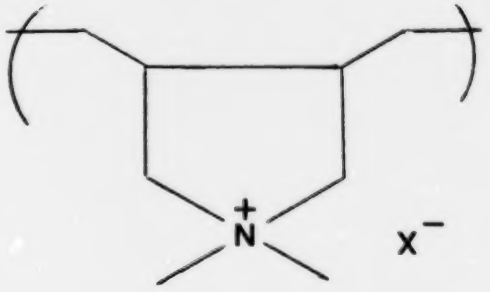
because of the presence of hydrolyzed amide as in structure 2, or cationic because of the presence of an amine or quaternized ammonium functionality, as in structure 3. Two anionic samples were identified

as sodium polyacrylate 4. The remaining cationic samples were identified as polyamines such as polyethyleneimine 5, quaternized



5 6

polyamines such as 6, or the structurally more complex quaternized polydiallyldimethylammonium salt 7.



7

1. Analysis of New Flocculant Samples

A total of six flocculants were received from the Scientific Authority for analysis during this stage of the contract. These were analyzed using the spectroscopic and wet chemical techniques developed during earlier stages of the contract, and the results are noted in

Table 2. Thus two samples, 4AS and WRL-N, were confirmed as neutral polyacrylamides. The WRL-N sample was found to have a high molecular weight, 21 million. Samples 97 and WRL-A were determined by spectroscopic analysis to be partially hydrolyzed polyacrylamides (see Figure 1 for an example of an infrared spectrum). Both samples were analyzed by conductometric titration and found too contain 27.3% and 30.4% hydrolyzed amide functionalities respectively.

Finally two flocculants, samples 96 and WRL-C, reported to be cationic in nature, were analyzed by a combination of spectroscopic analyses (see Figures 2 and 3 for infrared and nuclear magnetic resonance spectra) and colloid titration. Sample 96 was found to be a polyamine containing 9.3 milliequivalents per gram of weakly cationic functionality, among the highest levels of functionality observed. In addition, determination of this flocculant's molecular weight by low angle laser light scattering photometry (LALLSP) yielded a value of 15.2 million, the highest yet observed in this study for a polyamine flocculant. The WRL-C sample was found to be a cationic polyacrylamide with 0.32 milliequivalents of cationic functionality per gram, an unusually low figure.

2. New Analytical Methods

The cationic flocculants received by Raylo from the Energy, Mines and Resources, Western Regional Laboratory are usually slightly acidic in nature. This indicates that the cation amine-based functionality

must be neutralized and is therefore present as a salt. On the basis of a survey of the patent literature (2,3) and cost considerations, the most probable anion was expected to be chloride, therefore analyses of the chloride content of various cationic flocculants were carried out.

colourimetric silver nitrate titration procedure (4) was used, initially employing dichlorofluorescein as indicator. A series of polyamine based flocculants was analyzed by this method, and the chloride content compared to that expected from the colloid titration determination of total cationic functionalities, as noted in Table 3. These values are not expected to be identical unless unusual care had been taken in the neutralization or other treatments in their manufacture. However, four polyamines, samples 9, 53, 57 and 89, exhibited exceptionally large differences between their chloride and cation contents. Sample 53 has a pH of 8.6, indicating that much of the basic amine has not been neutralized, thereby accounting for the low chloride content. Samples 9 and 89, both of which also exhibit a substantially lower chloride content that expected on the basis of their polymeric cation content, must contain a different anion such as sulphate. The infrared spectra of both flocculants contain an absorption at 1100 cm^{-1}, indicative of sulphate. Sample 57, which contains excess chloride, contains added sodium cation corresponding to about 1.5 meg/g sodium chloride.

Analysis of a series of polyacrylamide-based cationic flocculants using the method discussed above yielded suspiciously low values for the chloride content, as noted in Table 4, apparently due to coagulation of the supposedly colloidal precipitate. A slightly modified colourimetric silver nitrate titration procedure employing potassium chromate as indicator (4) yielded more consistent results, as noted in Table 5. Two flocculants, samples 64 and 77, contained substantially more chloride than polymeric cationic functionality, indicating excess chloride salt had been added, whereas sample 92 appeared to contain an anion other than chloride.

Three of the 22 cationic flocculants examined by this technique, samples 57, 64 and 77, appeared to contain added chloride, in comparison to 15 of the 61 neutral and anionic flocculants which contained 5% or more added salt. This appears to reflect the greater difficulty in dissolving certain nonionic and anionic flocculants, as added inorganic salts assist in polymer dissolution (5).

Three flocculants, samples 9, 89 and 92, contain an anion other than chloride. This could be tentatively identified as sulphate in the first two flocculants from infrared spectra, however no conclusion as to the identity of the anion in sample 92 could be drawn.

3. Light Scattering Photometry

The effectiveness of polymers in flocculating suspensions has been found to be strongly dependent on polymer molecular weight, as illustrated in Figure 4 (6). This is in keeping with the physical bridging theory of suspension flocculation by polymers, illustrated in Figure 5 (7). The determination of the molecular weight characteristics of commercially available flocculants therefore represents an important goal of this project.

As discussed in the Flocculants Laser Light Scattering Evaluation Report, three methods widely used to determine the molecular weights of high molecular weight water soluble polymers were considered for flocculants. The simplest method, viscometric analysis (8), has the disadvantage that few reliable standards of polyacrylamides of suitably high molecular weight are available, and the viscometric parameters determined for polymers of low molecular weight cannot be safely extended to the very high molecular weight appropriate for the analysis of flocculants.

The second method, gel permeation chromatography (9), involves separation of the polymer molecules by size on a column of a material such as porous glass. In practice, the classical method of gel permeation chromatography requires that a series of standards of known molecular weight be injected to calibrate the system. In the absence of satisfactory standards the technique cannot be used to determine

absolute molecular weights. However, this technique remains important for the separation of a polymer sample by molecular weight to determine its molecular weight distribution.

The method of choice for polymer molecular weight determination is low angle laser light scattering photometry (LALLS) (10, 11). This method is based on the fact that polymer solutions scatter light far more effectively than a comparable solution of monomer or low molecular weight oligomers. This excess scattering, termed the excess Rayleigh factor R_θ, can be related to concentration and molecular weight by the following simplified equations:

$$R_\theta = kMwC \qquad \text{Equation 1}$$

$$Mw = R_\theta/kC \qquad \text{Equation 2}$$

where Mw is the weight average molecular weight, C is the polymer concentration, and K is a constant dependent on the optical and chemical properties of the polymer, which for low angle scattering and dilute aqueous solutions, equals 7.22×10^{-6} $(dn/dc)^2$. The ratio dn/dc is the polymer's differential refractive index or refractive index increment; the variation of the polymer solution's refractive index with concentration. The LALLS method allows the absolute molecular weight of a polymer to be determined without reference to standard samples of doubtful reliability.

Raylo therefore purchased the Chromatix KMX-6 LALLS photometer, and, as detailed in the previous Summary Report, has determined the molecular weights of over 50 flocculants, commercial polymer standards, and products of small-scale synthesis by Raylo personnel.

a) Assessment of the LALLS Method

Samples:

Dynamic LALLS photometry involves determination of the molecular weight of a large number of fractions of a polymer sample separated by molecular size by passage down a gel permeation column system. The number and weight average molecular weights of the sample are calculated from the equations:

$$Mn = \frac{\Sigma M_X N_X}{\Sigma N_X} \qquad \text{Equation 3}$$

$$Mw = \frac{\Sigma M_X W_X}{\Sigma W_X} \qquad \text{Equation 4}$$

where Mx is the molecular weight of a polymer with a degree of polymerization of x, N is the number of macromolecules of that size, and W is the weight fraction of macromolecules of that size out of the total.

In an effort to determine the reliability of the dynamic LALLS analytical procedure, two nonionic samples have been analyzed repeatedly and the results compared. The first sample, Polysciences 2806, a nonionic polyacrylamide standard, was analyzed on thirteen occasions. The second neutral polyacrylamide, Energy, Mines and Resources flocculant sample 4, was analyzed on ten occasions.

Expected polydispersity:

The polydispersity of the sample, that is, the ratio of weight average to number average molecular weight, represents a simple

estimate of the molecular weight distribution of the polymer. For instance, if a polymer is monodisperse, consisting entirely of molecules of the same molecular weight, the number and weight averages are equal, and the polydispersity equals 1. Conversely some polymerization methods yield polymers with polydispersities between 10 and 100 (8). Polyacrylamide polymerizations, which usually terminate by disproportionation, should theoretically have a polydispersity of 2. The observed polydispersity of the product of a single synthetic run should be within about 20% of this value. If a sample contained products of several different polymerization lots, each with a somewhat different molecular weight due to uncontrollable reaction variables, the polydispersity would further increase.

Erratic experimental results:

Four of the thirteen analyses of PS 2806 and two of the ten analyses of Sample 4 were unsatisfactory due to rapidly drifting or erratic output from one of the detectors. The nine remaining results obtained on sample PS2806 are shown in Table 6 and the eight results on sample Sample 4 are listed in Table 7. The results in these tables clearly contain outliers which have to be discarded before the remaining results can be averaged to obtain the best estimate of the values. Three analyses of PS2806 and one of the analyses of Sample 4 showed extreme polydispersity values. One of the analyses of Sample 4 gave a molecular weight that exceeded the other values by 50%,

therefore this run was excluded from further consideration.

Best estimation of weight average molecular weight and polydispersity:

The six remaining analyses of PS2806 had weight average molecular weights ranging from 5.82 to 8.72 million, with a mean of 7.21 million and a standard deviation of 1.17 million. The polydispersities varied from 1.70 to 2.62, with a mean of 2.24 and a standard deviation of 0.34. These results are close to the values expected for this polymer sample on the basis of earlier static LALLS analyses and theoretical considerations.

The six satisfactory analyses of sample 4 yielded weight average molecular weights between 6.33 and 8.57 million, with a mean of 7.32 million and a standard deviation of 0.77 million. Polydispersities ranged from 2.11 to 3.03, with a mean of 2.47 and a standard deviation of 0.41. The higher polydispersity observed for this commercial polymer, although within experimental error, may reflect a different polymerization procedure, however the mixing of production batches with slightly different molecular weight characteristics would produce the same result, as mentioned earlier.

Sensitivity of the computer program:

The consistency of the computer program for analysis of dynamic LALLS results has never been fully tested, although no obvious errors have been observed. Accordingly, minor alterations were made in the

data available to the computer originally from the last run noted in Table 7 and the average molecular weights and polydispersity recalculated by the computer. A slight alteration in the baseline of the refractometer resulted in increases in the weight average molecular weight from 7.18 million up to 10 million, although no significant alteration in polydispersity occurred. The sensitivity of the determined molecular weight to choice of baseline, a function normally carried out by the computer, indicates that a higher variability in the molecular weight determined by dynamic LALLS over that determined by static LALLS must be expected. The insensitivity of polydispersity to the choice of baseline, however, suggests that the molecular weight distribution can still be satisfactorily investigated.

Recommended procedure:

One third of the analyses carried out on these two polymers were judged unsatisfactory due to unstable chromatographic conditions of the detector traces. These results must, of course, be excluded from any estimates. The proportion of unsatisfactory analyses attributable to these causes will decrease as more experience is gained in the technique of dynamic LALLS photometry. Approximately one third of the remaining analyses were judged unsatisfactory because of surprisingly high weight average molecular weights or extreme values for the polydispersity of the sample. The use of triplicate analyses of each sample under investigation to obtain reliable results therefore appears

necessary.

4. KMX-6 LALLS Photometer Accessories

a) KMX-16 Differential Refractometer:

As discussed briefly earlier, the light scattering methods for the determination of weight average molecular weights are based on the fluctuation theory of light scattering which correlates the Rayleigh scattering with molecular weight in the manner shown below (11):

$$Kc/R_\theta = 1/Mw + 2A_2C \qquad \text{Equation 5}$$

$$K = (2\pi n^2/\lambda^4 \quad N)\,(dn/dc)^2\,(1 + \cos^2\theta) \qquad \text{Equation 6}$$

where dn/dc is the differential refractive index of the solute-solvent system at the wavelength of light used. Such dn/dc data are quite scarce in literature reports and those that are available are usually not measured at the wavelength of light generated by the He-Ne laser in the KMX-6 photometer. Furthermore, the polymer under investigation must be positively identified before the appropriate dn/dc can be obtained from the literature and determination of its molecular weight carried out.

In practice, estimates of the dn/dc values of a series of cationic flocculants were made based on the very few reported dn/dc analyses of related polyamines and polyacrylamides (12). The dn/dc's of these flocculants were then determined on a Chromatix KMX-16 Differential Refractometer by Dr. J.M. Wilson of Halliburton Services. The results noted in Table 8 clearly indicate that estimation of dn/dc can only

product values with a 15% uncertainty, an error that will result in a 30% deviation of the determined molecular weight.

The Chromatix KMX-16 Differential Refractometer was accordingly purchased. The instrument has been calibrated and has produced satisfactory analyses of PS2806 polyacrylamide standard, yielding values between 0.14 and 0.15, close to literature values of 0.142 and 0.146 (12). Future molecular weight analyses will employ dn/dc data produced by this instrument. If sufficient time is available the dn/dc values of flocculants previously analyzed with the KMX-6 photometer will be obtained, and any corrections to the molecular weights reported earlier will be made.

b) Digital Correlator:

Polymeric flocculant performance is sensitive to the concentration and identity of ions in solution. Both of these variables affect the molecular size of polymer molecules (13) and thus their effectiveness, as the macromolecules ability to form interparticle bridges decreases as their size decreases.

The measurement of the molecular size has been carried out by viscometric means (14), however the method of choice involves measurement of the translation diffusion coefficients (D_T) which can be related to the molecular size by using the Stokes Einstein equation:

$$a = kT/6\ \pi\ \eta\ D_T \qquad \text{Equation 7}$$

where a is molecular radius, K is Boltzman's constant, T is temperature

and η is solvent viscosity. The most effective technique at present for determination of diffusion coefficients is quasielastic light scattering (QLS), also known as photon correlation spectroscopy (15).

Accordingly, Raylo has recently purchased the Chromatix Digital Correlator accessory to the KMX-6 photometer which will allow the very high speed data acquisition required for quasielastic light scattering determinations of molecular size. Analysis of known latex standards has commenced, indicating that data acquisition by the digital correlator and data handling by the LSI-11 microcomputer are operating satisfactorily. Due to the late (March 1982) arrival of the final components of the digital correlator, there was insufficient time to commence analysis of polymeric standards and flocculants.

c) Type PW GPC Columns:

The separation of hydrophilic cationic polymers by molecular weight on most gel permeation column systems has failed due to sample retention by the silica-based column. Chemical modification of the surface of silica packing by bonding quaternary ammonium groups can eliminate this difficulty, but such packings are not commercially available (16). Recently, however, Varian Type PW columns, manufactured by Toya Soda, have yielded good results with a series of cationic polymers (17). Therefore three columns of this type, sizes 3000, 4000 and 5000, were ordered and have been received.

The column most suitable for resolution of high molecular weight

polymers, PW5000, has been extensively tested. Nonionic polyacrylamides, Polysciences 2806 standard sample and flocculant sample 4, cationic polyacrylamide flocculant samples 10, 23 and 95, and cationic polyamine samples 6 and 91, were investigated. The analysis of the neutral polymers produced highly erratic results as noted in Table 9, suggesting that these polymers may be poorly separated on the column. This pattern was also observed in cationic polyacrylamides with molecular weights above 5 million, suggesting that polymers with excessively high molecular weights may be above the column's most effective range of analysis. In contrast, sample 95 and sample 91, a cationic polyamine flocculant, yielded less erratic results for molecular weights below 5 million.

The upper limit of size resolution of a gel permeation column corresponds to the point at which all molecules are excluded from the pores of the packing material (18). Thus in Diagram 1, molecule A is small enough to be resolved, whereas molecules B and C, although of very different size, are both excluded from all pores in the packing material, and would be eluted at the same time. To estimate the upper exclusion limits of a column, the molecular weight of sample eluted is plotted against the elution time, and the point at which the curve indicates little further change in elution time with increasing molecular weight is taken as the exclusion limited, as illustrated in Diagram 2.

Diagram 1: Steric exclusion of large macromolecules.

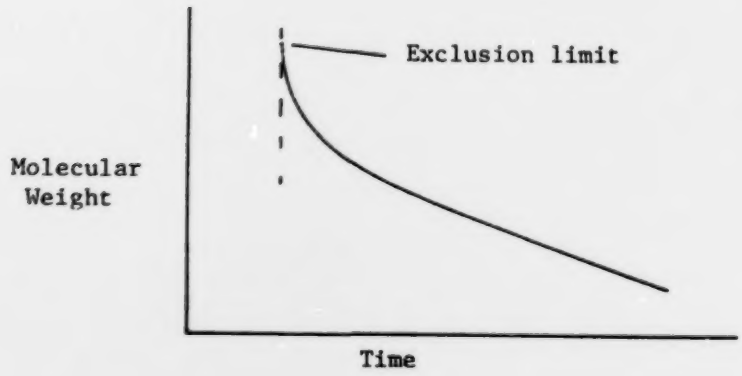


Diagram 2: Determination of column exclusion limit.

Such a procedure typically yielded a curve such as that shown in Figure 6, in which a definite change in the slope of the curve is apparent near 10 million molecular weight. This suggests that polymers that contain a substantial fraction of molecules with molecular weights above 10 million may yield unsatisfactory analyses upon integration of all of the results in the computer.

II. DEGRADATION OF POLYACRYLAMIDE-BASED FLOCCULANTS IN SOLUTION

1. Investigation of Chemical Stabilizers

As discussed earlier, the molecular weight of high molecular weight polymeric flocculants is strongly correlated with their flocculating ability, so it is important to avoid chemical conditions capable of degrading the polymeric backbone. Such degradation has been observed upon oxidation by ozone (19), however such harsh conditions are unlikely to occur in industry.

Free radical attack is generally believed to be the cause for the chemical degradation of high molecular weight polyacrylamide-based polymers (20). The oxidation of ferrous to ferric ion by air is believed to involve the formation of hydrogen peroxide (21), as shown in reactions 1 and 2. A mixture of hydrogen peroxide and ferrous salt

$$FeOH^{+} + O_2 + H^{+} \longrightarrow FeOH^{2+} + HO_2^{\bullet} \qquad (1)$$

$$Fe^{2+} + HO_2^{\bullet} + H_2O \longrightarrow FeOH^{2+} + H_2O_2 \qquad (2)$$

constitutes Fenton's reagent, a potent free radical oxidant of organic compounds. By analogy to other free radical degradations (22, 23), the initial step is probably formation of the very reactive hydroxyl radical, followed by hydrogen abstraction from the polymer backbone:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + HO^{\bullet} \qquad (3)$$

$$CH_2\text{-}\underset{\displaystyle R}{\underset{|}{CH}}\text{-}CH_2\text{-} + HO^{\bullet} \longrightarrow CH_2\text{-}\underset{\displaystyle R}{\underset{|}{\dot{C}}}\text{-}CH_2\text{-} + H_2O \qquad (4)$$

Subsequent reaction with oxygen will yield a peroxy radical, which is quenched by hydrogen abstraction:

$$-CH_2\text{-}\underset{\displaystyle R}{\underset{|}{\dot{C}}}\text{-}CH_2\text{-} + O_2 + R'H \longrightarrow CH_2\text{-}\underset{\displaystyle R}{\overset{\displaystyle O_2H}{\underset{|}{\overset{|}{C}}}}\text{-}CH_2\text{-} + R'^{\bullet} \qquad (5)$$

Such hydroperoxides typically cleave on exposure to ferrous salts to yield a degraded product (5):

$$-CH_2\text{-}\underset{\displaystyle R}{\overset{\displaystyle O_2H}{\underset{|}{\overset{|}{C}}}}\text{-}CH_2\text{-} \xrightarrow{Fe^{2+}} -CH_2\text{-}\underset{\displaystyle R}{\underset{|}{C}}{=}O + HO^{\bullet} + {}^{\bullet}CH_2\text{-} \qquad (6)$$

The presence of an oxidizable metal ion and oxygen in the polymer solution are necessary to allow initiation of these or other analogous free radical reactions.

The previous Summary Report discussed studies conducted on the nonionic flocculant sample 4 (or Superfloc N-127) which indicated that ferrous salts did indeed degrade polyacrylamides, although the degradation could be markedly reduced by the addition of certain chemical stabilizers. These studies were greatly expanded to include other potential stabilizers and both anionic and cationic polyacrylamide-based flocculants in this phase of the contract.

Assessment of the extent of degradation was usually based on the variation of the specific viscosity of the polymer solution over time. This can be related to molecular weight by the following relationships. For slow degradation, it has been shown that (25):

$$1/Mw\ (t) = 1/Mw\ (0) + Kt/2 \qquad \text{Equation 8}$$

where Mw is the weight average molecular weight initially and at time t, and K is the first order rate constant for chain scission. Molecular weight, on the other hand, is related to intrinsic viscosity as shown:

$$[\eta] = k\ Mv^{a} \qquad \text{Equation 9}$$

where a is dependent on the nature of the polymer and solvent, usually falling between 0.65 and 1. Mv is the viscosity-average molecular

weight defined by the equation (8):

$$Mv = \frac{\Sigma M_x^{1+a} \; Nx}{\Sigma M_x \; N_x} \qquad \text{Equation 10}$$

where x, M and N are as previously defined. If the value of a is assumed to be close to 1, and as intrinsic viscosity is approximately proportional to specific viscosity of a given polymer at a constant concentration, equation 8 can be rewritten in terms of specific viscosity as the approximation:

$$1/\eta(t) = 1/\eta(0) + K't \qquad \text{Equation 11}$$

$$\eta(0)/\eta(t) = 1 + K''t \qquad \text{Equation 12}$$

where K' and K'' are proportional to the rate of degradation. Therefore if the inverse of the specific viscosity is plotted against time, a line with a slope of K' results. A similar format in which all initial values are normalized to 1 (see equation 9) will be used here to illustrate the effects of degradation.

A 0.1% solution of the polymer under investigation was prepared, and the appropriate salt added - usually 50 ppm ferrous ion from ferrous sulphate. In most cases 200 ppm of a chemical stabilizer under investigation was also added. The specific viscosities of the samples over a one month period were measured with a Cannon-Fenske capillary viscometer. Both the anionic flocculant sample 39 (Perastol 2810) and the cationic sample 95 (Calgon M515) were examined less intensively than the nonionic sample 4 (Superfloc N-127) as initial studies of the

three flocculants showed similar behaviour.

The effect of several free radical inhibitors and other potential chemical stabilizers on the rate of degradation of nonionic polyacrylamide solutions by 50 ppm ferrous sulphate was investigated and the results are noted in Table 10 and shown in part in Figures 7 and 8. A substantial reduction in the rate of degradation was observed for solutions stabilized by 200 ppm of thiourea, allyl alcohol, furan, isopropanol or formaldehyde. The most effective chemical stabilizer consisted of a 2:1 mixture of thiourea and isopropanol. Acidification to pH 2 also reduced changes in specific viscosity, whereas raising the pH to 10 actually increased the solution specific viscosity over time. This last result can be attributed to hydrolysis of the nonionic polymer to the much more viscous partially hydrolyzed polyacrylamide. Several other potential stabilizers including ascorbic acid, ethylenediaminetetraacetic acid, and pyrogallol produced a more rapid decrease in viscosity than ferrous ion alone.

The uncertainty of the relationship between the specific viscosity of the polymer solution and the actual molecular weight suggested the need for absolute molecular weight determinations. Accordingly, the degraded polyacrylamide solutions, after passage down an cation exchange column to remove the iron salts, were analyzed by dynamic low angle laser light scattering (LALLS) photometry. The weight average molecular weights of degraded samples noted in Table 10 correlated well

with specific viscosity with the exception of the basic solution (see Figure 9). Most of the low viscosity polymer solutions had molecular weights below the minimum required for the gel permeation system to give satisfactory analyses, but all were below one million.

For 0.1% solutions of nonionic polyacrylamide, if the results for the basic solution are excluded and all of the undefined low molecular weights assumed to approximate that of EDTA- stabilized polymer, linear regression analysis indicated the following relationship with a correlation coefficient of 0.973:

$$\eta_{sp} = 1.616 \times 10^{-1} \; Mw \qquad \text{Equation 13}$$

The activity of the various chemicals used as stabilizers depends on their structure. Thus alcohols and monofunctional unsaturated stabilizers such as formaldehyde and furan, all of which could be oxidized by the free radical system thereby protecting the polymer, were effective. Thiourea may operate as a stabilizer in this manner, or possibly in a manner similar to allylthiourea, a closely related chemical, which has been reported to act as a scavenger for perhydroxyl radical ($HO_2^{\cdot}$) thereby preventing the formation of hydrogen peroxide as noted in Reaction 2 above (26). Allylthiourea also appears to react directly with hydrogen peroxide (27), thereby destroying the product as well as the reagent of Reaction 2.

All chemicals containing carboxylic acid functionalities, especially those with the capability to act as bidentate or

multidentate ligands such as EDTA and ascorbic acid, caused an increase in the rate of degradation. Similarly, pyrogallol catalyzed rapid polymer degradation. The catalytic effect on ferrous autoxidation by salicylic acid derivatives (28) and dihydroxyaromatic derivatives (29) has been shown to be attributable to acceleration of the electron transfer process from the ligand co-ordinated ferrous ion, causing an increase in the rate of Reaction 1. Our investigations of this phenomenon will be discussed shortly.

The investigation of anionic sample 39 (Perastol 2810) and cationic sample 95 (Calgon M515) under similar conditions yielded similar results, as noted in Tables 11 and 12 respectively, and illustrated in Figures 10 and 11. The overall rate of degradation did appear to depend on the charge on the polyacrylamide backbone, as the positively charged cationic polymer exhibited the lowest rate followed by the nonionic polyacrylamide. The anionic partially hydrolyzed polyacrylamide degraded most rapidly, possibly due to its ability to chelate with and thereby activate the ferrous ion. The dependence of the final inverse viscosity ratio on the nature of the polyacrylamide is illustrated in Figure 12.

The solutions of degraded anionic sample 39 were investigated by dynamic LALLS photometry and traces of high molecular weight polymer

detected, resulting in a comparatively high weight average molecular weight. On the other hand, the bulk of the polymer and hence the number average molecular weight was substantially below that of the original polyacrylamide sample as noted in Table 13. Accordingly the polydispersities of several of the degraded polymer solutions greatly exceeded the usual values between 2 and 3. As no directly analogous mechanism in aqueous free radical chemistry could be found, further research into this phenomenom should be carried out if discussions with the Scientific Authority so decide.

2. Dependence of Degradation on the Concentration of Stabilizer and Ferrous Salt

In order to more accurately reflect the conditions likely to be encountered in commercial applications of flocculants, the effects of a lower concentration of ferrous sulphate and a lower concentration of the most effective stabilizer, thiourea-isopropanol, on the degradation were investigated. In addition, the coal washery waters in Alberta usually contain substantial amounts of certain ions, in particular calcium and sulphate (30). Therefore degradation studies in the presence of 320 ppm calcium sulphate were carried out. The variation of solution specific viscosity was, as usual, used to assess the extent of polyacrylamide degradation.

The results of these studies are noted in Table 14 and illustrated in Figure 13. If ferrous salt was excluded, little degradation was

observed - that is, the ratio of initial to final viscosity was very close to 1. The presence of 50 ppm ferrous salt raised this value to about 3, indicating that the average polymer molecule had been degraded into three fragments, attributable to an average of 2 backbone cleavages per macromolecule. The presence of only 10 ppm ferrous salt caused a proportionally smaller amount of degradation, with an intial/ final viscosity ratio of 1.36. This would correspond to an average of 0.36 backbone cleavages per molecule, approximately one fifth of the value observed with the more concentrated ferrous salt solution. Similarly, a solution containing 50 ppm ferrous salt stabilized by 20 ppm thiourea-isopropanol showed an initial/final viscosity ratio of 1.91, corresponding to 0.91 backbone cleavages per macromolecule, whereas a similarly stabilized solution containing only 10 ppm ferrous salt, the ratio decreased to 1.24, attributable to an average of 0.24 cleavages per polymer molecule. Reducing the concentration of iron salts therefore caused a similar decrease in the rate of degradation, and this effect was unaltered by the presence of calcium sulphate or stabilizer.

The concentration of the stabilizer, thiourea-isopropanol, was varied between 200 ppm and 2 ppm. The results noted in Table 14 clearly indicated the greater effectiveness of higher concentrations of stabilizer, but also show that about 20 ppm stabilizer reduced degradation to less than half of its original value in 50 ppm ferrous

salt solutions, from 2.05 to 0.91 backbone cleavages per molecule. Similar results were obtained for solutions containing 10 ppm ferrous salt and low concentrations of stabilizers, however 20 ppm did not appear to be quite as effective as at higher ferrous salt concentration. The use of 50 ppm thiourea-isopropanol did markedly reduce degradation.

The degradation of Superfloc N-127 in the presence of 320 ppm calcium sulphate closely parallelled the behaviour of the salt-free solutions with one minor exception. As shown in Figure 13 the viscosity ratio of a solution containing 10 ppm ferrous salt and 50 ppm stabilizer rose slowly initially, indicating some slight degradation, and then fell, suggesting that an increase in molecular weight was occurring, an unlikely event. The viscosity ratio of the corresponding solutions containing calcium sulphate rose slowly throughout the experiment, suggesting that the unusual behaviour of the salt free solution is attributable to experimental error or unexpected chemical change in the later stages of the experiment. An extrapolated final value of 1.18 for the viscosity ratio of the calcium free solution has been given for comparison.

The rate of degradation of nonionic polyacrylamide flocculant has been found to be directly related to the concentration of ferrous salt in solution, and to be essentially unaffected by the presence of 320 ppm calcium sulphate, a typical salt concentration in Alberta coal

washery waters. Furthermore, between 20 ppm and 50 ppm of stabilizer was sufficient to halve the rate of degradation as measured by viscometry for the solutions studied. The addition of 5% by weight of such a chemical stabilizer to a dry flocculant would yield a 25 ppm stabilizer solution at typical flocculant usage levels (1 pound flocculant per ton of effluent water). The added chemical cost, at most 30¢ per pound of flocculant, may not be excessive if free radical polymer degradation is found to be occurring.

3. Dependence of Degradation on the Identity of the Oxidant

The importance of both dissolved oxygen and ferrous ion in the degradation of polyacrylamide in solution has been discussed. The presence of oxygen alone is clearly insufficient for degradation, as oxygen was not excluded from any of the degradation studies thus far carried out. The effect of iron in the absence of oxygen was tested.

A series of 0.1% polymer solutions was prepared using degassed and nitrogen flushed water. All procedures were carried out in a glove bag flushed with nitrogen. Several test solutions for each set of conditions were prepared, so that after measurement of solution viscosity, that sample was discarded.

The results, as noted in Table 15, showed essentially no change in viscosity over one month whether or not ferrous salt was present. Oxygen therefore is the ultimate source of the oxidizing species, rather than any trace organic or inorganic peroxides present in the

polymer, as suggested by some workers (31).

Known quantities of hydrogen peroxide were injected into two series of oxygen free solutions, and as noted in Table 16, a rapid decline in viscosity took place, followed by a plateau. This suggests that if ferrous ion and hydrogen peroxide are present together, they rapidly degrade the polymer. This in turn indicates that the formation of hydrogen peroxide from ferrous ion and oxygen must be the rate-limiting step in the degradation of polyacrylamide.

In order to investigate this reaction further, the change of hydrogen peroxide concentration over time in different reaction mixtures was monitored using a spectrophotometer determination of the yellow colour of the titanium-hydrogen peroxide complex (32). This method yielded reproducible hydrogen peroxide analyses of clear solutions to concentrations of less than 0.5 ppm in most cases.

Thus analyses of an iron-free polyacrylamide solution containing 15 ppm hydrogen peroxide indicated that a very slow decrease in peroxide concentration occurred (see Table 17). A similar polyacrylamide solution to which 50 ppm ferrous sulphate had been added contained only 1 ppm hydrogen peroxide after one hour, and 0.5 ppm after 24 hours. Thus the ferrous salt increased the rate of degradation of hydrogen peroxide by a factor of 50 or more. A similar disappearance of hydrogen peroxide is noted if no polyacrylamide is present in the peroxide-ferrous salt solution. In this case, the

products of the degradation should be oxygen and water.

Thus far, the results of the investigation of the proposed two-step oxidative degradation of polymers by oxygen and iron salts suggest that the first step, formation of hydrogen peroxide from dissolved oxygen, is much slower than either of the two pathways of peroxide depletion, therefore it can be considered the rate determining step. This suggests two methods for the prevention of degradation; exclusion of oxygen, which has already been shown to be effective, or addition of chemical stabilizers which interfere with the free radical reactions responsible for the appearance of hydrogen peroxide.

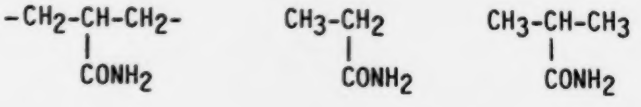
Any increase in the rate of peroxide formation should, on the other hand, lead to greater degradation of the polymer. This may account for the greatly increased rate of polyacrylamide degradation when either pyrogallol, a phenolic oxygen scavanger, or ethylene-diaminetetraacetic acid (EDTA), an iron chelating agent, were tested as potential stabilizers. Both have been reported to accelerate the reaction of molecular oxygen and ferrous iron (28, 29). Conversely, amines were not found to be activating agents, suggesting that they may be useful as chemical stabilizers.

4. Model Studies of Polyacrylamide Degradation

The proposed mechanism for the oxidative free radical degradation suggests fragments of polymer would terminate in ketone, alcohol, or related oxygenated functionalities. In order to confirm the mechanism

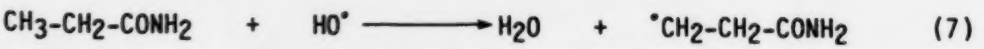
of degradation noted above, determination of the functionalities in the products of degradation would be of value. However, the small number of polymer backbone cleavages required to yield the observed decreases in molecular weight, less than one per 10,000 monomer units, make analysis of the end-groups of the degraded polymers extremely difficult. Therefore attempts to parallel the degradation of the polymer backbone using a more concentrated free radical system and a low molecular weight model of polyacrylamide were initiated.

Although there is evidence indicating that the perhydroxide ($HO_2^{\bullet}$) or superoxide ($O_2^{\bullet-}$) radicals may be implicated in degradative reactions (33), the hydroxyl radical ($HO^{\bullet}$) is usually held responsible for initiating degradaton, as discussed above. Therefore Fenton's reagent, a known generator of hydroxyl radicals, was chosen for the study (34). Either propionamide 9 or isobutyramide 10, either of which fairly closely resemble the polyacrylamide 8 could be employed as model compounds, and ultimately both were used in the study.



8 9 10

The experimental procedure (35) used a 0.4 M solution of Fenton's reagent. The expected product of the free radical oxidation of propionamide would be adipamide, as shown here:



$$2 \quad {}^{\bullet}CH_2\text{-}CH_2\text{-}CONH_2 \longrightarrow H_2NCO\text{-}(CH_2)_4\text{-}CONH_2 \qquad (8)$$

The products of the reaction were separated by elution from a silica gel chromatography column. Examination of the infrared and nuclear magnetic resonance spectra of each fraction indicated that although the majority of the propionamide was unchanged, a substantial number of different products had been formed. Attempts to cleanly separate the different products by repeated column chromatography were unsuccessful, making identification of the individual products of the reaction impossible.

At least two free radicals were probably formed from the substrate in this reaction. Thus in addition to hydrogen abstraction from the terminal methyl, abstraction from the methylene to give the radical 12 must occur.

$${}^{\bullet}CH_2\text{-}CH_2\text{-}CONH_2 \qquad\qquad CH_3\text{-}\dot{C}H\text{-}CONH_2$$

11 12

Each of these radicals can couple to like radicals to yield adipamide or 2,3-dimethylsuccinamide respectively, to each other to yield 2-methylglutaramide, or to the hydroxyl radical to produce hydroxypropionamide. The spectral evidence suggests all of these may be present, in addition to other unidentified products.

Isobutyramide 10 was treated under similar conditions, however little evidence of any reaction could be detected. The only spectral evidence consistant with any of the most likely products appeared in

the nuclear magnetic resonance spectrum of the largely unaltered product of the reaction, in which a weak methyl resonance appeared. This singlet is likely to be due to the resonance of the four symmetrical methyl groups of tetramethylsuccinamide, the dimerization product present in a concentration about 1% of the largely unaltered starting material.

The observed extent of degradation does indicate that the hydrocarbon backbone resists hydroxyl radical attack fairly well, and usually forms products of simple coupling when radical atack does occur, as illustrated here:

$$2\ RH \xrightarrow{HO^{\bullet}} 2\ R^{\bullet} + 2H_2O \longrightarrow R\text{-}R \qquad (9)$$

$$RH \xrightarrow{HO^{\bullet}} R^{\bullet} + H_2O \xrightarrow{HO} ROH \qquad (10)$$

One crucial difference between this model study of polyacrylamide degradation is in the relative concentration of dissolved oxygen compared to that of free radicals. In the model study a high concentration of free organic radicals would favour coupling as illustrated by reaction 9, whereas the extremely low radical concentration during the degradation of polyacrylamide would allow competing reactions between such radicals and dissolved oxygen to predominate:

$$R^{\bullet} \xrightarrow{O_2} RO_2^{\bullet} \longrightarrow \text{oxidation products} \qquad (11)$$

The effect of high concentrations of oxygen on the product distribution of similar model studies in the future may be investigated to determine if such a side reaction can be detected.

III. SYNTHESIS AND POSTMODIFICATION OF POLYMERS

1. Synthesis of 2,4- and 3,4-ionene

Approximately half of the cationic flocculants commercially available in Canada are based on chemically modified polyacrylamides, the remainder being loosely categorized as polyamines. These include polyethyleneimine, polydiallyldimethylammonium chloride (PDADMAC), quaternized poly(epichlorohydrin), and linear polyquaternary salts termed ionenes (36). Certain of these can be copolymerized with each other or, in the case of PDADMAC, with polyacrylamide.

The majority of polyamine flocculants examined in this contract have been tentatively identified as ionenes by infrared and nuclear magnetic resonance spectroscopy. Exact identification has not been possible without standard materials of known structure, which are not presently available commercially. The synthesis of certain ionenes reportedly employed as flocculants (37) was therefore undertaken.

The usual method for synthesis of ionenes involves the reaction of equimolar amounts of N,N,N',N'-tetramethyldiaminoalkane and dibromo-

alkane in a suitable organic solvent, as shown here (38). Thus 0.05 mole of both tetramethylethylenediamine (X = 2) and tetramethyl-

$$(CH_3)_2N\text{-}(CH_2)_x\text{-}N(CH_3)_2 \quad + \quad Br(CH_2)_yBr \longrightarrow \quad (12)$$
$$\text{-}(\overset{+}{N}(CH_3)_2\text{-}(CH_2)_x\text{-}\overset{+}{N}(CH_3)_2\text{-}(CH_2)_y\text{——})_n \cdot 2\ Br$$

propyldiamine (X = 3) were reacted with 0.05 mole dibromobutane in 30 ml of 1:1 methanol:dimethylformamide under the conditions noted in Table 18, and ionene products isolated.

The 2,4-ionene, prepared by stirring the reagents at room temperature for four days, was formed in 95% yield. The infrared spectrum, shown in Figure 14, exhibited the expected absorptions, although substantial water was present in the cast of polymer (3400 and 1650 cm^{-1}). The nuclear magnetic resonance spectrum originally indicated the presence of 10% impurity (2.8 ppm, quartet), but precipitation of an aqueous sample in acetone yielded a purified product whose spectrum is shown in Figure 15. The integration of the four strong proton resonances confirmed the proposed structure of the 2,4-ionene.

The 3,4-ionene was prepared by two methods, the first of which employed the same conditions as the 2,4-ionene synthesis, and gave quantitative yield. The second procedure, reflux of the reaction mixture for 24 hours, yielded two insoluble fractions. The first

product, an easily filtered solid, was obtained in 73% yield. Precipitation of the remaining low molecular weight polymer by addition to excess acetone yielded a further 19% product.

The infrared and nuclear magnetic resonance spectra of the initial 3,4-ionene product of the high temperature procedure are shown in Figures 16 and 17 respectively. With the exception of two absorptions at 3500 and 1640 cm^{-1} attributable to water, and a weak absorption at 2050 cm^{-1} attributable to protonated amine the infrared spectrum is consistent with an ionene structure. The integration of the nuclear magnetic resonance spectrum confirms the identity of the polymer as a 3,4-ionene.

The molecular weights of the different ionene products were investigated by both viscometry and static LALLS photometry. The Mark-Houwink equation for 3,4-ionene bromides in 0.3M potassium bromide solution has been reported as (38):

$$[\eta] = 2.94 \times 10^{-4} M^{0.61} \qquad \text{Equation 14}$$

Although a small discrepancy can be expected in employing this relationship in the molecular weight determination of 2,4-ionene bromides, the viscometric and LALLS determined molecular weights agreed fairly well (see Table 18), indicating that the 2,4-ionene bromide was of comparatively lower molecular weight. The molecular weight of

3,4-ionene bromide exceeded the 2,4-ionene bromide, whatever the method of preparation. Thus the lower molecular weight fraction of the product prepared under reflux conditions possessed a molecular weight of approximately 10,000, whereas the products that precipitated from the methanol:diemthylformamide solvent during both synthetic procedures possessed molecular weights between 25,000 and 50,000. As the product of the procedure employing reflux conditions needed no purification whereas the product of the room temperature procedure required precipitation from acetone, the first procedure is the one of choice for the synthesis of small samples of 3,4-ionene.

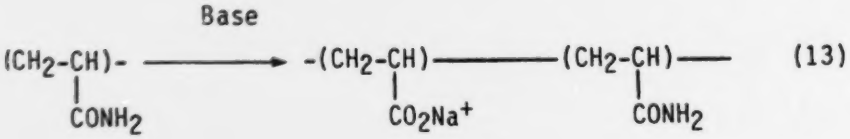
The infrared and nuclear magnetic spectra of the two ionenes were compared to those of polyamine flocculants previously investigated during this contract. While similarities were noted, no flocculant spectra completely matched those of the synthetic products. Therefore no flocculant thus investigated is simply 2,4- or 3,4-ionene. Their presence as copolymers remains a possibility.

2. Postmodification of Acrylamide to Organic Soluble Polymers

The determination of molecular weight of water soluble polymers such as polyacrylamides is a relatively unexplored field. Accordingly, many experimental difficulties have been encountered that have signficiantly increased the time required for polymer analysis. As the related polymer poly(methylacrylate) has been studied in detail in certain organic solvents, the chemical conversion of polyacrylamide-

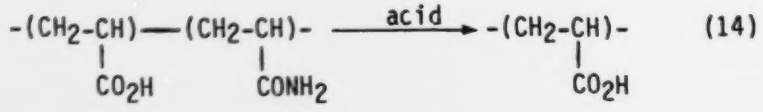
based polymers to poly(methylacrylate) via a polyacrylic acid intermediate was undertaken.

Two methods of hydrolysis to polyacrylic acid are widely used for polyacrylamide-based polymers. Basic hydrolysis, the most widely employed (39) has the advantage that it rapidly converts polyacrylamide with a low or intermediate degree of hydrolysis to a largely hydrolyzed product, with about 75% carboxylate content (see Reaction 13).



(13)

Acid hydrolysis causes extensive crosslinking due to imide formation at intermediate levels of hydrolysis, however if continued for longer times, degrees of hydrolysis up to 95% have been reported with hydrolysis of the undesired imide (40). The rate of dilute acid hydrolysis, however, is extremely low for pure polyacrylamide requiring at least 25% carboxylic acid functionalities initially present on the backbone to achieve complete hydrolysis even after 300 hours (see Reaction 14):



(14)

Neutral polyacrylamides were therefore partially hydrolyzed with 0.2M potassium hydroxide. All partially hydrolyzed polyacrylamides were then passed down a Rexyn 101 cation exchange column, yielding a mildly acidic solution. This solution was then refluxed for approximately 300 hours to produce polyacrylic acid.

The polyacrylic acid was concentrated in water, and diluted with about 10 volumes of 1:1 tetrahydrofuran:methanol, a convenient solvent for both polyacrylic acid and poly(methylacrylate). Addition of an excess of diazomethane in ether converted the polyacrylic acid smoothly into the methyl ester, as shown in Reaction 15:

$$-(CH_2\text{-}CH)- \xrightarrow{CH_2N_2} -(CH_2\text{-}CH)- \qquad (15)$$

$$\qquad\quad | \qquad\qquad\qquad\quad |$$

$$\qquad CO_2H \qquad\qquad\quad CO_2CH_3$$

In order to usefully employ this transformation in polymer molecular weight analysis, however, the resistance of the polymer backbone to any degradation during the two stages of chemical transformation must be assessed.

Determination of intrinsic viscosities of certain poly(methylacrylate) samples prepared from well characterized polyacrylamides suggested the polymer's molecular weight had decreased during the chemical reactions, as noted in Table 19. Molecular weight analysis of

these samples by dynamic LALLS photometry using tetrahydrofuran as solvent did indeed yield values far below those of the original polyacrylamide and somewhat below those determined viscometrically, indicating that some degradation of molecular weight has occurred during the two-step chemical transformation of polyacrylamide to poly(methylacrylate).

Esterification of polyacrylic acid by diazomethane has been used previously as a gentle non-degradative method to give poly(methylacrylate) (41). On the other hand, acid hydrolysis at elevated temperatures has been found to cause degradation of commercially produced polyacrylamides, possibly due to traces of residual impurities (42). The acid hydrolysis of polyacrylamides therefore appears to be an unsatisfactory procedure, and any further attempts to produce poly(methylacrylate) will have to employ different hydrolytic conditions.

IV. FRACTIONATION OF POLYMERS

The importance of high molecular weight in polymeric flocculants has repeatedly been stressed in this report. In practical terms, however, the advantages of extremely high molecular weight polymers must be balanced with the difficulties of synthesis, handling, and use under industrial conditions. For instance, proper dissolution of a flocculant of 10 million molecular weight can take up to 24 hours, and normally requires strong stirring or agitation which could degrade the

polymer. A low molecular weight flocculant, on the other hand, may be totally ineffective. It was therefore decided in discussions with the Scientific Authority that a co-operative testing program in which Raylo prepared polymers of various molecular weights for flocculation testing by Energy, Mines and Resources personnel would be undertaken.

1. Fractional Precipitation

A quantity of sample 4 was fractionated by addition of the non-solvent methanol to an aqueous solution (43), as discussed in the preceeding Summary Report, and the various fractions noted in Table 20 turned over to Energy, Mines and Resources personnel after determination of their molecular weight. Determination of the flocculating efficiency of these samples indicated that little increase in flocculating efficiency occurred above about 3 million molecular weight (44). If this observation is confirmed in other similar tests, a major change in the priorities of properties of flocculants for coal washeries may be required.

2. Controlled Polyacrylamide Fragmentation by Ultrasonic Irradiation

Attempted fractional precipitation of several flocculants in the manner described above yielded poor results.

The feasibility of controlled degradation of flocculant samples of known molecular weight by ultrasonic irradiation of solution was therefore investigated. Such irradiation of an aqueous solution that contains dissolved gases produces large numbers of small transient

bubbles or cavities (45). The high shear in the solution immediately adjacent to such cavitation is believed to be largely responsible for the observed degradation of polymer in solution, as illustrated in Diagram 3. Thus smaller macromolecules will be able to withstand the high shear forces of cavitation (Diagram 3a to 3b), whereas larger macromolecules will be cleaved (Diagram 3b to 3c).

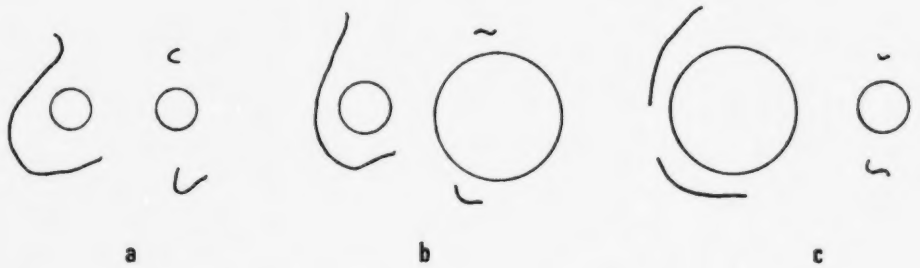


Diagram 3: Effect of ultrasonic cavitation on macromolecules in solution.

Furthermore, as high shear stress normally causes breakage of macromolecules larger than a certain critical size dependent on the shear stress (46), the molecular weight distribution of the polymer should narrow during ultrasonic irradiation.

A series of 0.1% solutions of Polysciences nonionic polyacrylamide standard PS2806 were subjected to ultrasonic irradiation from a Biosonic IV ultrasonic generator, manufactured by Bronwill Scientific.

The polymer solutions were subjected to irradiation for times up to about 10 minutes at a variety of power settings ranging up to about 10 watts. The molecular weight of the polyacrylamide was then investigated by dynamic LALLS photometry and the results noted in Tables 21 and 22 and illustrated in Figures 18 and 19.

The ultrasonic irradiation decreased the polymer molecular weight as a function of the increasing power used, and the molecular weight fell linearly with the logarithmic increase of time. The results obtained using the 40 and 80 power settings shown in Figures 18 and 19 exhibited a very clear cut decline over time.

The molecular weight distributions of the degraded samples usually showed little difference from that of the undegraded polyacrylamide, with the exception of a few that exhibited a much wider distribution than expected. This can be attributed to the non-uniform degradative conditions in the sonicated solution (46).

Ultrasonic degradation of nonionic polyacrylamide solutions has been successfully used to produce samples of lower molecular weight in a controlled manner. Procedures will be developed to employ this degradative method in the production of small quantities of polyacrylamides of any desired molecular weight.

CONCLUSIONS

The techniques of spectrophotometric and wet chemical analysis developed for flocculant analysis allow rapid determination of the physical, chemical, and molecular weight properties of samples under investigation. Application of these techniques to additional flocculant samples received during this phase of the contract highlighted the unusual nature of sample 96, a polyamine with both high cationic functionalities and high molecular weight.

Investigation of the free radical oxidative degradation of nonionic, anionic, and cationic polyacrylamide flocculants found that certain common antioxidants such as pyrogallol and ascorbic acid actually increase degradation by activation of the metal salt, whereas thiourea and certain alcohols can greatly reduce degradation. Studies of the effects of various concentrations of thiourea-isopropanol indicated that the addition of stabilizers sufficient to halve the rate of degradation would cost less than 30¢ per pound.

Comparison of cationic flocculants with samples of quaternized ionene polymers prepared at Raylo indicated no flocculant was a simple ionene homopolymer. The possibility that some incorporate ionenes as copolymers must be investigated.

PRESENT AND FUTURE WORK

The major effort in the near future will attempt to determine the solution properties of all types of flocculants in the presence of various cations. The bulk of analyses will be carried out using the Digital Correlator accessory to the KMX-6 Laser Photometer to determine the translational diffusion coefficient and hence the size of the macromolecule in solution. Efforts to correlate this to viscosity measurements of the flocculants will be made. The dependence of macromolecular size on the presence and concentration of apparently minor constituents of coal washery waters is expected to explain heretofore inexplicable phenomena.

Degradation studies of various flocculants will continue, with the aim of determining what the probable causes of degradation in normal washery operations are.

The synthesis of polymer standards will continue, and as soon as clear indications of the nature of the structure-activity relationship of flocculants is elucidated, synthesis of an "ideal: flocculant commenced.

REFERENCES

1. A. Benedek and A.E. Hamielec, Proc. Chem. Indust. Can.; Flocculation and Dispersion Symposium, p.189, 1974.

2. S. Gutcho, "Waste Treatment with Polyelectrolytes and other Flocculants", Noyes Data Corporation, Park Ridge, New Jersy, 1977.

3. J. Vostrcil and F. Juracka, "Commercial Organic Flocculants", Noyes Data Corporation, Park Ridge, New Jersey, 1976.

4. A.I. Vogel, "Quantitative Inorganic Analysis", Second Edition, p.251, Longmans, Green and Co., New York, 1951.

5. A.E. Hamielec, Raylo Consultant, personal communication.

6. W.F. Linke and R.B. Booth, Trans. AIME, 217, 367 (1960).

7. W.K. Le Mer and T.W. Henley, "Nature of the Flocculation Reaction in Solid-Liquid Separations", Solid-Liquid Separations, Chapter 3, HMSO, London, 1966.

8. N.G. Billingham, "Molar Mass Measurements in Polymer Science", p.1 and p.172, John Wiley & Sons, New York, 1977.

9. Reference 8, p.199.

10. Reference 8, p.105.

11. R.C. Jordan, J. Liquid Chromatog., 3, 439 (1980).

12. Chromatix Application Notes LS-1 through LS-10, 1976 - 1979; R.C. Jordan, personal communication.

13. C. Tanford, "Physical Chemistry of Macromolecules", p.490, John Wiley & Sons, New York, 1961.

14. Reference 13, p.399.

15. R.J. Berne and R. Pecora, "Dynamic Light Scattering", Wiley Interscience, New York, 1976.

16. C.P. Talley and L.M. Bowman, Anal. Chem., 51, 2239 (1979).

17. P.L. Dubin and I.J. Levy, Polymer Preprints, 22, 132 (1981).

18. N.C. Billingham, "Practical High Performance Liquid Chromatography", Chapter 10, p.167, Ed. C.F. Simpson, Heyden and Sons Ltd., London, 1976.

19. J. Suzcki, H. Harada, and S. Suzuki, J.Appl. Polym. Sci., 24, 999 (1979).

20. R.D. Shupe, 55th Annual SPE Conference, Dallas, Texas, 1980.

21. S. Fallah, Angew. Chem. Int. Edit., 6, 496 (1967).

22. C. Walling and R.A. Johnson, J.Am.Chem.Soc., 97, 2405 (1975).

23. J.F. Rabek, "Comprehensive Chemical Kinetics", Vol. 14, Chapter 4, p.280, Elseviers, New York, 1975.

24. D. Swern, "Organic Peroxides", Vol. 2, p.103, Wiley Interscience, New York, 1971.

25. H. Vink, Makromal Chemie, 63, 105 (1964).

26. P. Alexander and M. Fox, Nature, 170, 1022 (1952).

27. A. Weissler, J.Am.Chem.Soc., 81, 1077 (1959).

28. T. Kaden, D. Walz and S. Fallab, Helv. Chim. Acta., 43, 1639 (1960).

29. T. Kaden and S. Fallab, Helv. Chim. Acta., 44, 714, (1961).

30. N. Andersen, Energy, Mines and Resources, personal communication.

31. H.C. Haas and R.L. MacDonald, Polymer Letters, 10, 461 (1972).

32. G.M. Eisenberg, Ind. Eng. Chem., Anal. Ed., 15, 327 (1943).

33. J.M. Gebichi and B.H. Bielski, J.Am.Chem.Soc., 103, 7020 (1981).

34. J.R. Lindsay-Smith and R.O.C. Norman, J.Chem.Soc., 2897 (1963).

35. D.D. Coffman, E.L. Jenner and R.D. Lipscomb, J.Am.Chem.Soc., 80, 2864 (1958).

36. F. Halverson and H.P. Panzer, Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Vol. 10, p.489, John Wiley & Sons, New York, 1980.

37. D. Casson and A. Rembaum, Polymer Lett., 8, 773 (1970).

38. A. Rembaum and H. Noguchi, Macromolecules, 5, 261 (1972).

39. J. Moens and G. Smets, J. Polymer Sci., 23, 931 (1957).

40. G. Muller, J.C. Fenyo and E. Seligny, J.Appl. Polym. Sci., 25, 627 (1980).

41. A. Katchalsky and H. Eisenberg, J. Polymer Sci.,, 6, 145 (1951).

42. G. Muller, Polymer Bulletin, 5, 39 (1981).

43. J.F. Rabek, "Experimental Methods in Polymer Chemistry", p.63, John Wiley & Sons, New York, 1980.

44. H. Hamza, Energy, Mines and Resources, personal communication.

45. A. Weissler, Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Edition, Vol. 20, p.773-791, Interscience, New York, 1969.

46. A.H. Abdel-Alim and A.E. Hamielec, J. Appl. Polym. Sci., 17, 3769 (1973).

TABLE 1

Chemical and ionic classification of flocculants previously analyzed.

Structure	Ionic Classification			
	Anionic	Cationic	Nonionic	Total
Polyacrylamide	54	23	10	87
Polyacrylic acid	2	--	--	2
Polydiallydimethylammonium salt	--	4	--	4
Polyamine	--	9	--	9
Total	56	36	10	102

TABLE 2

Physical and chemical properties of six flocculants.

Sample	Type	% Volatiles	Functionality	% Salt
4AS	PAM	5.3	0% hydrolysis	0
96	PA	61.0	9.3 meq/g	-
97	PAM-PH	0.9	27.3% hydrolysis	5.5
WRL-N	PAM	8.7	0% hydrolysis	0
WRL-A	PAM-PH	7.6	30.4% hydrolysis	3.5
WRL-C	PAM-C	6.9	0.32 meq/g	-

PA : polyamine
PAM : polyacrylamide
PH : partially hydrolyzed
C : cationic

TABLE 3

Chloride content of certain polyamine flocculant samples compared to total polymeric cation.

Sample	Chloride (meq/g)	Cation (meq/g)
6	6.03	4.2
9	6.95	11.2
14	6.27	5.2
16	6.99	6.8
20	7.77	6.2
53	1.15	5.1
56	7.26	5.5
57	8.56	4.6
86	4.65	4.8
89	2.72	6.4
91	5.07	6.7
94	6.92	6.6

TABLE 4

Comparison of the chloride content and the total polymeric cation of certain polyacrylamide-based cationic flocculants by the unsatisfactory dichlorofluorescein method.

Sample	Chloride (meq/g)	Cation (meq/g)
10	1.66	2.3
22	6.71	4.1
25	0	1.1
62	1.05	0.6
63	0	2.4
64	0	1.4
70	0	1.3
71	0	1.1
74	0	0.4
75	1.66	1.3
77	0	1.5
85	0	0.7
90	2.00	3.3
92	0	1.2
95	4.56	2.5

TABLE 5

Comparison of the chloride content and the total polymeric cation of certain polyacrylamide-based cationic flocculants using potassium chromate indicator.

Sample	Chloride (meq/g)	Cation (meq/g)
10	1.92	2.3
23	0.06	0.0
62	1.14	0.6
63	2.26	2.4
64	3.42	1.4
74	0.09	0.4
75	1.83	1.8
77	5.54	1.6
85	0.08	0.7
92	0.09	1.2

TABLE 6

Dynamic LALLS determination of molecular weight and polydispersity of Polysciences polyacrylamide 2806.

Molecular Weight (millions)		
Number Average	Weight Average	Polydispersity
2.97	4.32	1.46*
2.67	5.82	2.20
3.54	7.87	2.25
3.07	8.07	2.62
5.13	8.72	1.70
4.46	6.90	1.55*
2.67	6.22	2.32
2.81	11.1	3.95*
2.80	6.55	2.34

* Extreme values of polydispersity.

TABLE 7

Dynamic LALLS determination of molecular weight and polydispersity of flocculant sample 4

Molecular Weight (millions)		
Number Average	Weight Average	Polydispersity
2.73	6.33	2.32
2.55	7.46	2.93
3.61	7.60	2.11
2.23	6.77	3.03
4.08	8.57	2.10
4.46	12.61	2.83*
2.28	3.50	1.53*
3.13	7.18	2.30

* Excluded from calculation of average result.

TABLE 8

Estimated and actual differential refractive indices (dn/dc) for certain cationic flocculants.

Sample	Estimate	Actual	Error (%)
10	0.146	0.163	12
88	0.146	0.151	10
9	0.149	0.160	7
14	0.149	0.146	2
PDADMAC	0.149	0.168	13
PEO	0.136	0.132	3

TABLE 9

Determination of polymer molecular weight by dynamic LALLS and static LALLS

Sample	PW 5000		Mw (static)
	Mw	Standard Deviation	
PS2806	13.9	6.11	6.4*
4	6.8	2.15	7.6*
10	17.5	4.91	7.9
23	17.9	8.03	14.7
95	6.3	0.37	4.5
6	8.4	1.00	12.1
91	0.68	--	0.97

* Dynamic LALLS results, 4 column CPG set.

TABLE 10

Normalized specific viscosity, weight average molecular weight, and the inverse of normalized specific viscosities of 0.1% polyacrylamide solutions after 790 hours in the presence of certain cations and stabilizers.

Sample	η/η_0	Mw (millions)	η_0/η
No Salt	1	6.0	1
Na	0.81	---	1.23
Ca	0.91	---	1.10
Co(II)	0.91	---	1.10
Ce(II)	0.36	2.4	2.75
Fe(II) pH 10	1.67	4.3	0.60
Fe(II) pH 2	0.74	5.3	1.35
Fe(II) Furan	0.65	4.8	1.54
Fe(II) Formaldehyde	0.52	3.3	1.93
Fe(II) Thiourea	0.78	5.4	1.28
Fe(II) Thiourea/IPA	0.93	4.6	1.08
Fe(II) IPA	0.60	3.9	1.67
Fe(II) Allyl alcohol	0.82	4.6	1.22
Fe(II) Glyoxal	0.39	2.2	2.60
Fe(II) Sodium Formate	0.22	1.6	4.6
Fe(II) Glyoxylic acid	0.18	low	5.52
Fe(II) Mercaptoacetic acid	0.11	low	9.0
Fe(II) Ascorbic acid	0.07	low	15.0
Fe(II) TMPDA	0.07	low	15.0
Fe(II) EDTA	0.06*	0.4	17.0
Fe(II) Pyrogallol	0.06	low	17.0

* Specific viscosity
TMPDA = N,N,N',N'-Tetramethylphenylenediamine.

TABLE 11

Ratio of final to initial specific viscosity after 760 hours for partially hydrolyzed polyacrylamide in the presence of 50 ppm ferrous salt and certain chemical stabilizers.

Sample	η/η_0	η_0/η
No Salt	0.80	1.25
Fe(II)	0.22	4.47
Fe(II) pH 9	0.94	1.06
Fe(II) pH 3	0.27	3.71
Fe(II) Furan	0.27	3.74
Fe(II) Thiourea	0.42	2.37
Fe(II) Formaldehyde	0.31	3.24
Fe(II) EDTA	0.08	12.5
Fe(II) Pyrogallol	0.02	50

* Final specific viscosity.

TABLE 12

Ratio of final to initial viscosity after 700 hours of cationic polyacrylamide in the presence of 50 ppm ferrous salt and certain chemical stabilizers.

Sample	η/η_0	η_0/η
No Salt	0.93	1.07
Fe(II)	0.68	1.48
Fe(II) pH 9	0.60	1.68
Fe(II) pH 3	0.93	1.07
Fe(II) Furan	0.76	1.32
Fe(II) Thiourea	0.87	1.15
Fe(II) Formaldehyde	0.68	1.48
Fe(II) EDTA	0.25	5.0
Fe(II) Pyrogallol	0.03	32.0
Fe(II) Sodium Sulphite	0.52	1.92
Fe(II) Isopropanol	0.67	1.49

TABLE 13

Dynamic LALLS of ferrous ammonium sulphate degraded solutions of partially hydrolyzed polyacrylamide flocculant sample 39.

Solution	Mn (Millions)	Mw (Millions)	Polydispersity
No Salt	2.94	4.73	1.61
Fe(II)	0.86	7.84	9.12
Fe(II) pH 9	1.77	3.43	1.94
Fe(II) pH 3	0.52	1.40	2.69
Fe(II) Furan	1.47	6.19	4.21
Fe(II) Formaldehyde	1.46	6.82	4.67
Fe(II) Thiourea	2.72	5.62	2.07
Fe(II) EDTA	Low*	Low*	--

* Molecular weight below detection limits of about 0.5 million.

TABLE 14

Changes in the initial/final viscosity ratio of solutions of sample 4 (Superfloc N-127) over 670 hours in the presence of certain additives, and approximate assessment of the degradation in terms of cleavages per macromolecule.

Fe(II) (ppm)	Thiourea/IPA (ppm)	CaSO (ppm)	(initial) (final)	Degradation
-	--	---	1.06	0.06
-	--	320	1.02	0.02
50	--	---	3.05	2.05
50	--	320	3.20	2.20
50	200	---	1.08	0.08
50	20	---	1.91	0.91
50	20	320	1.71	0.71
50	5	---	2.27	1.27
50	2	---	2.23	1.23
10	--	---	1.36	0.36
10	--	320	1.42	0.42
10	50	---	1.06 (1.18)	0.06 (0.18)
10	50	320	1.23	0.23
10	20	---	1.24	0.24

* Extrapolated value from first 400 hours observations.

TABLE 15

Specific viscosity of solutions of polyacrylamide flocculant sample 4 after exposure to ferrous salts with exclusion of oxygen for certain times (hours).

Solution	3	27	99	333	501	640
No Salts	1.88	1.80	2.02	1.84	1.98	1.82
Fe(II)	1.78	1.76	1.72	1.66	1.70	--
Fe(II) + Thiourea	1.76	1.80	1.78	1.76	1.76	1.70

TABLE 16

Effect on solution viscosity of addition of hydrogen peroxide to a ferrous salt-containing solution of sample 4.

Peroxide Conc. (ppm)	Before Addition	1 hour	280 hours
20	1.78	0.08	0.08
10	1.78	0.18	0.18

TABLE 17

Decrease in the concentration (ppm) of hydrogen peroxide over time in the presence and absence of 50 ppm ferrous ion and 0.1% Superfloc N-127 (sample 4) from an initial concentration of 15 ppm.

Solution	Time (hrs)				
	1	5	24	48	72
#4	15	13.7	--	--	10.7
#4, Fe(II)	1	--	0.5	0.5	--
Fe(II)	0.5	--	0.2	0	--

TABLE 18

Synthesis and molecular weight distribution of synthesized ionene polymers.

Ionene	Method	Yield (%)	Mw (viscometry)	Mw (LALLS)
2-4	a	95	2,500	3,300
3-4	a	100	56,000	27,800
3-4	b-1	73	49,000	48,000
	b-2	19	9,800	14,800

a; 4 days stirring at room temperature.
b; 1 day stirring at reflux
b-1; precipitated from reaction mixture.
b-2; precipitated by addition to acetone.

TABLE 19

Molecular weight of polyacrylamide (PAM) and chemically derived poly(methylacrylate).

Sample	PAM Mw (millions)	Poly(methylacrylate) LALLS	Mw (millions) Viscometry
4	7.60	0.81	2.07
Alc-3	8.93	0.67	1.95

TABLE 20

Molecular weights of a fractionated polymer.

Sample	Average Molecular Weight (millions) Viscosity	Light Scattering
Flocculant 4	4.56	16.80
Fraction 1	2.89	9.57
Fraction 2	2.45	approx. 4.8
Fraction 3	1.59	3.13
Fraction 4	insufficient sample	
Fraction 5	0.91	2.16

TABLE 21

Molecular weight of PS2806 after treatment with ultrasonic radiation at 40 power setting for varying items.

Time (seconds)	Molecular Weight (millions)
0	6.1
30	5.2
120	4.0
180	3.2
310	2.6
600	2.5
1380	0.8

TABLE 22

Molecular weight of PS2806 after treatment with ultrasonic radiation at 80 power setting for varying times.

Time (seconds)	Molecular Weight (millions)
0	6.1
10	5.2
20	4.8
20	4.8
30	3.4
30	3.0
60	3.1
60	3.0
120	2.6
240	1.7
300	0.9
600	0.3

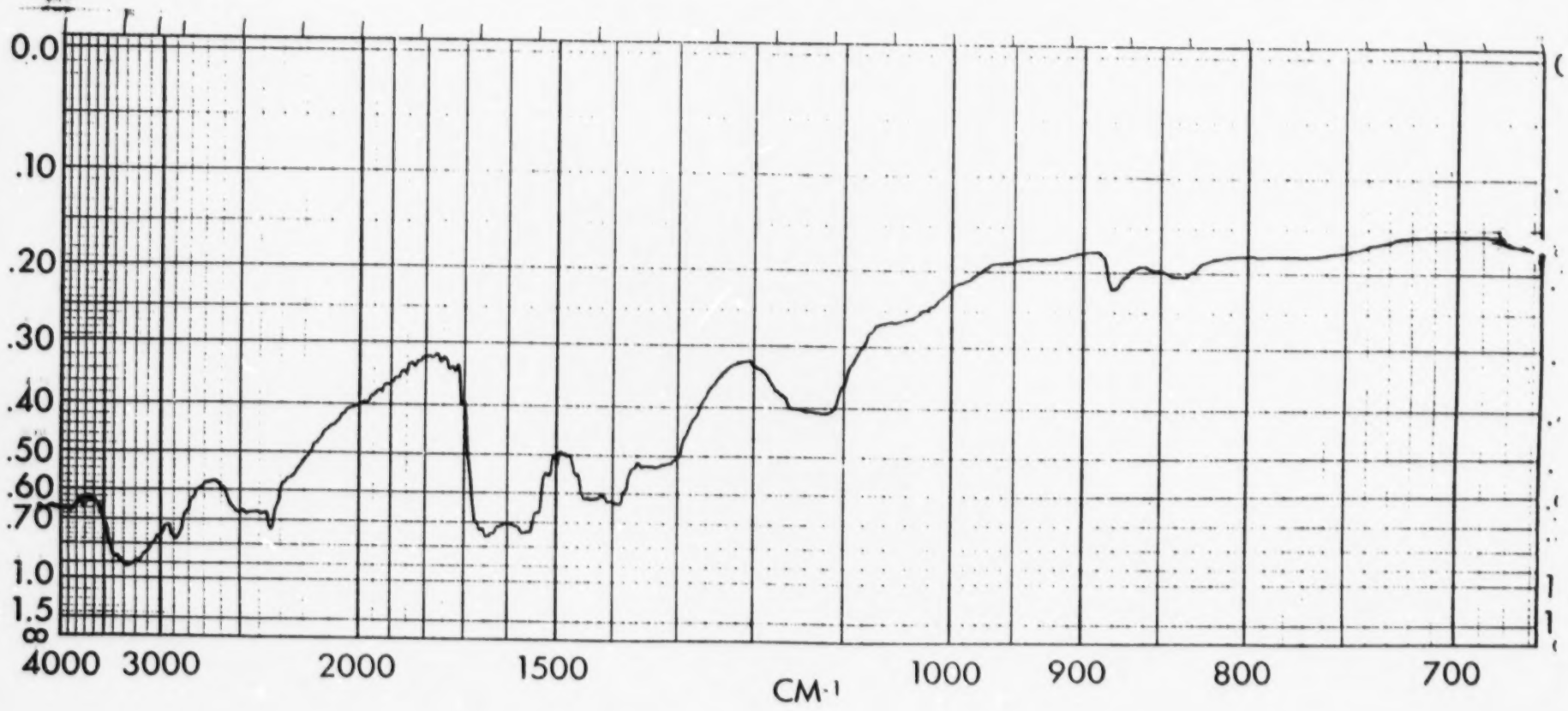


Figure 1 : Infrared spectrum of sample 97.

3400 - 3100 cm^{-1}; N-H

1650 cm^{-1}; amide

1550 cm^{-1}; carboxylate

1400 cm^{-1}; C-H, carboxylate

2900 cm^{-1}; C-H

1600 cm^{-1}; amide

1440 cm^{-1}; C-H

1130 cm^{-1}; C-N, sulphate

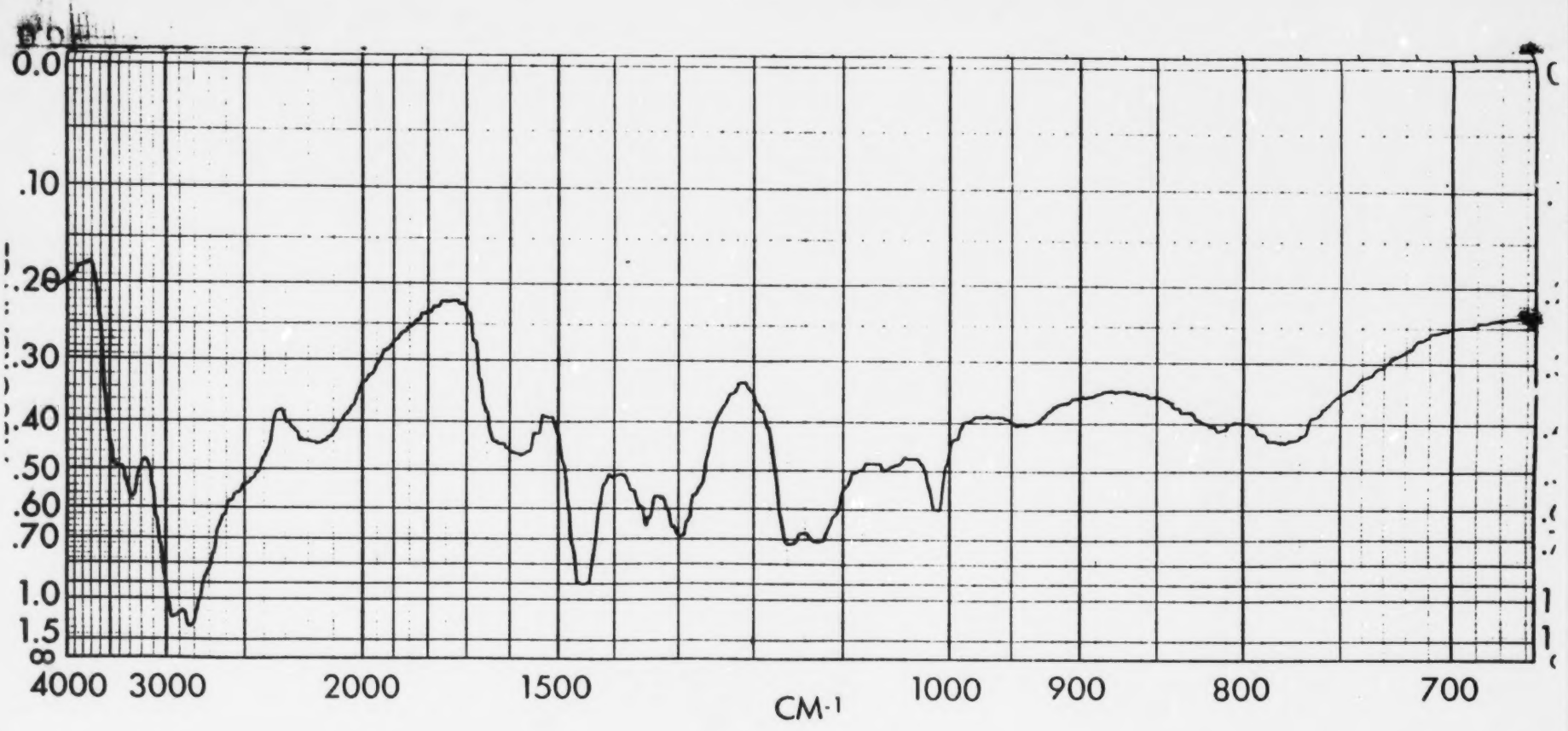


Figure 2 : Infrared spectrum of sample 96 (aqueous cast)

3400 - 3200 cm^{-1}; N-H

2800 - 2000 cm^{-1}; $\overset{+}{N}$-H

1450 cm^{-1}; C-H

2900 cm^{-1}; C-H

1600 cm^{-1}; N-H

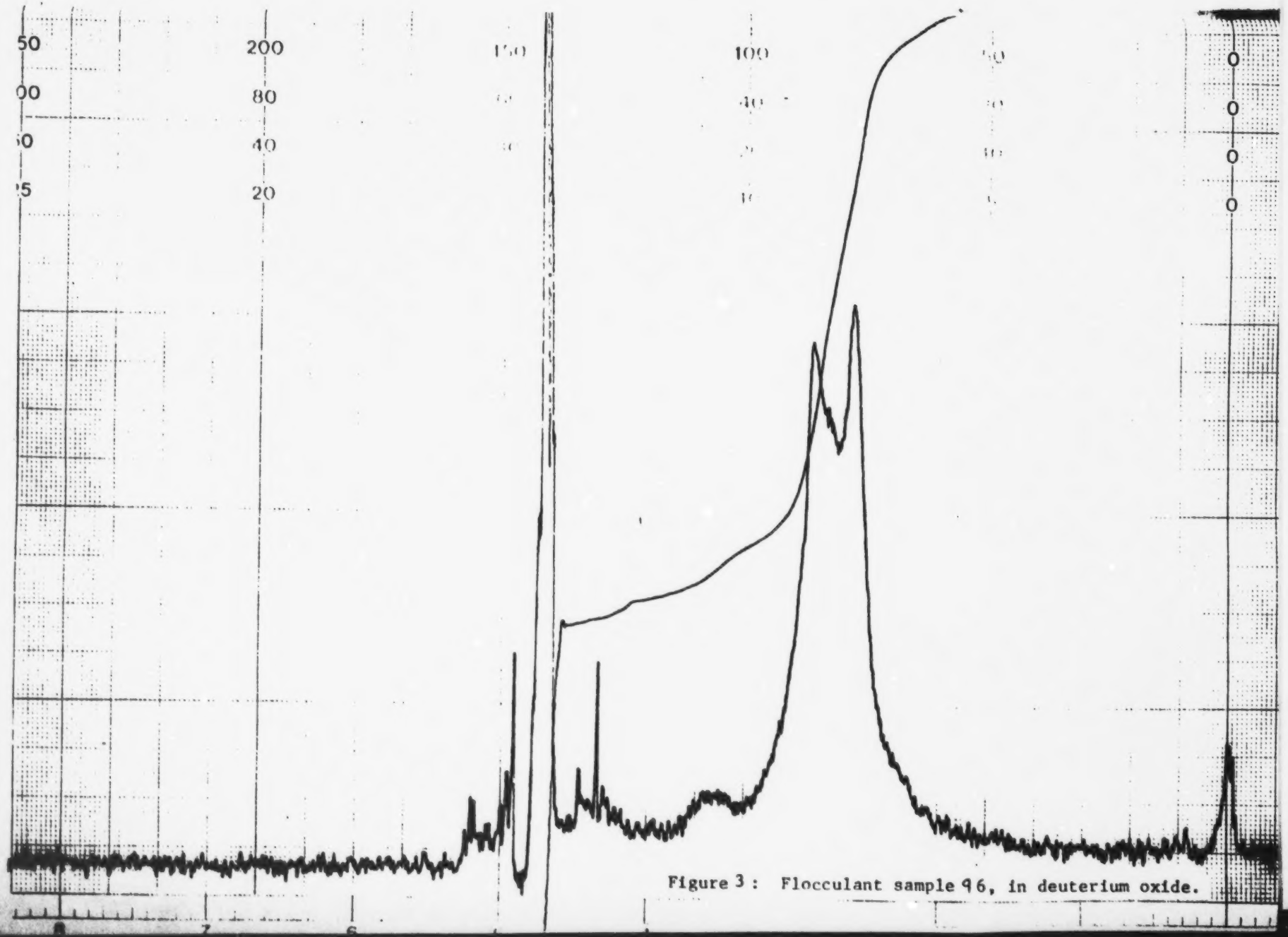


Figure 3 : Flocculant sample 96, in deuterium oxide.

Figure 4:

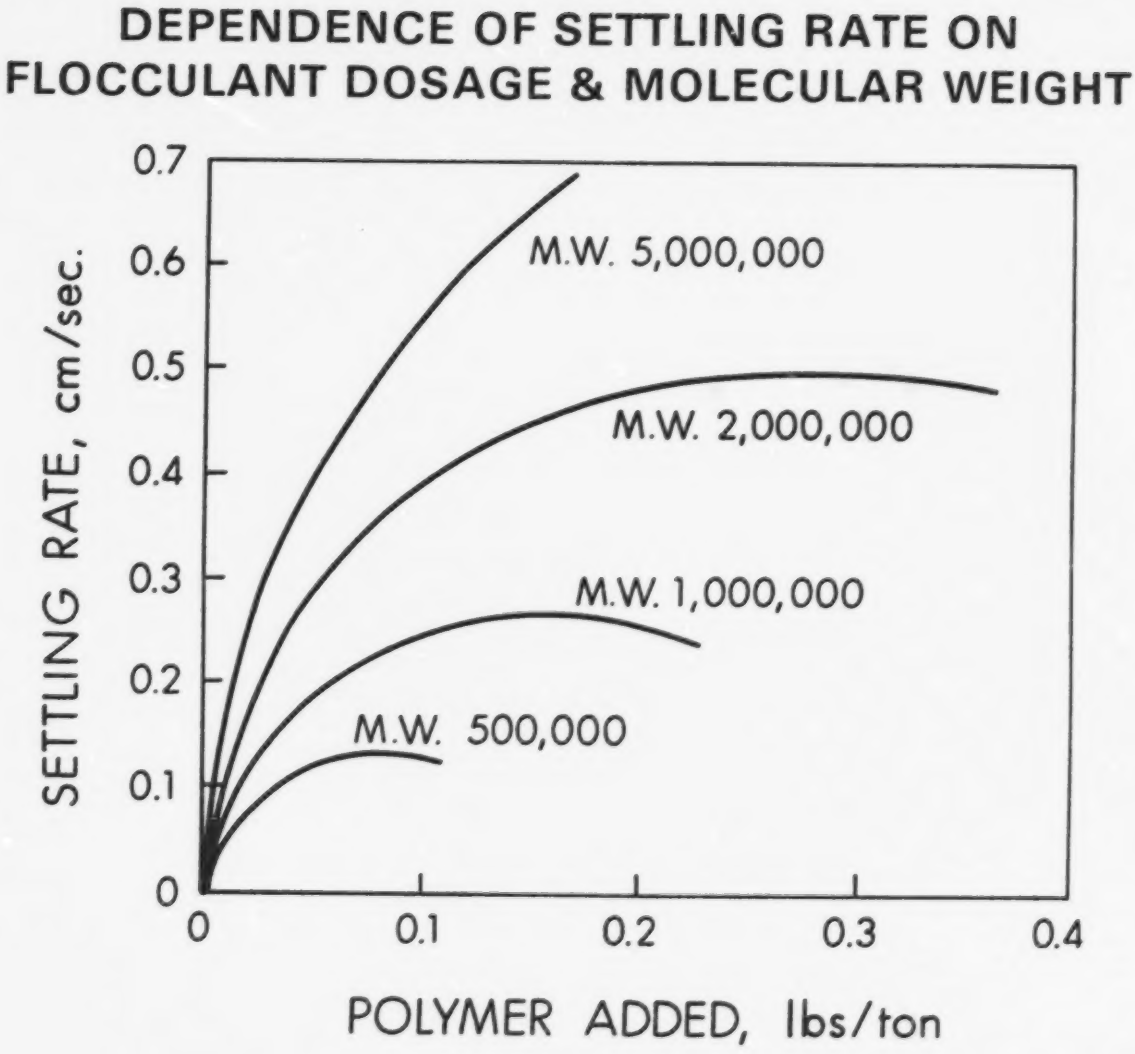
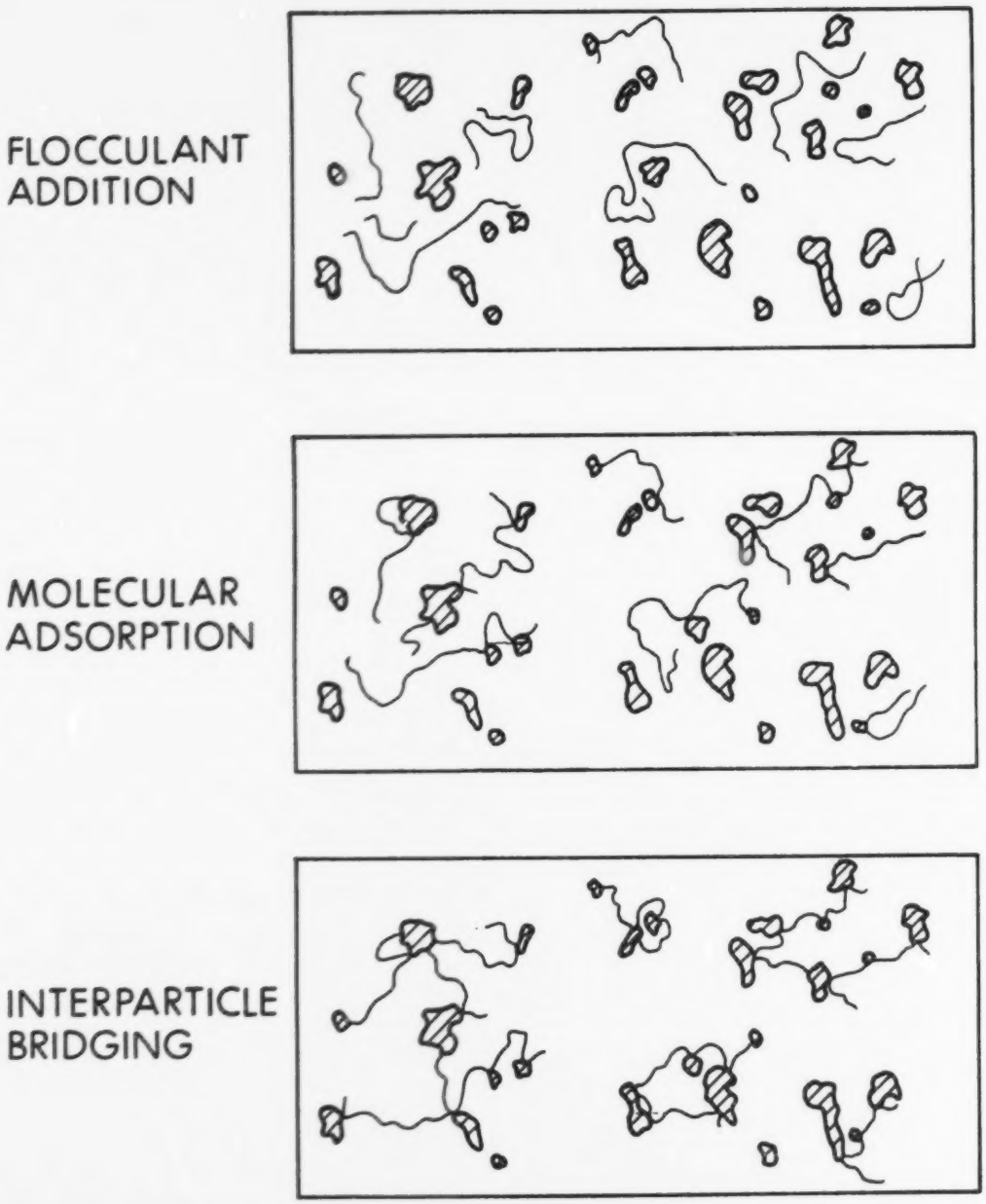

DEPENDENCE OF SETTLING RATE ON
FLOCCULANT DOSAGE & MOLECULAR WEIGHT
SETTLING RATE, cm/sec.
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
M.W. 5,000,000
M.W. 2,000,000
M.W. 1,000,000
M.W. 500,000
0
0.1
0.2
0.3
0.4
POLYMER ADDED, lbs/ton

Figure 5:

BRIDGING MECHANISM OF FLOCCULATION



FORMATION OF A FLOC

Figure 6: Molecular weight of different fractions of polyacrylamide PS2806 at increasing elution times.

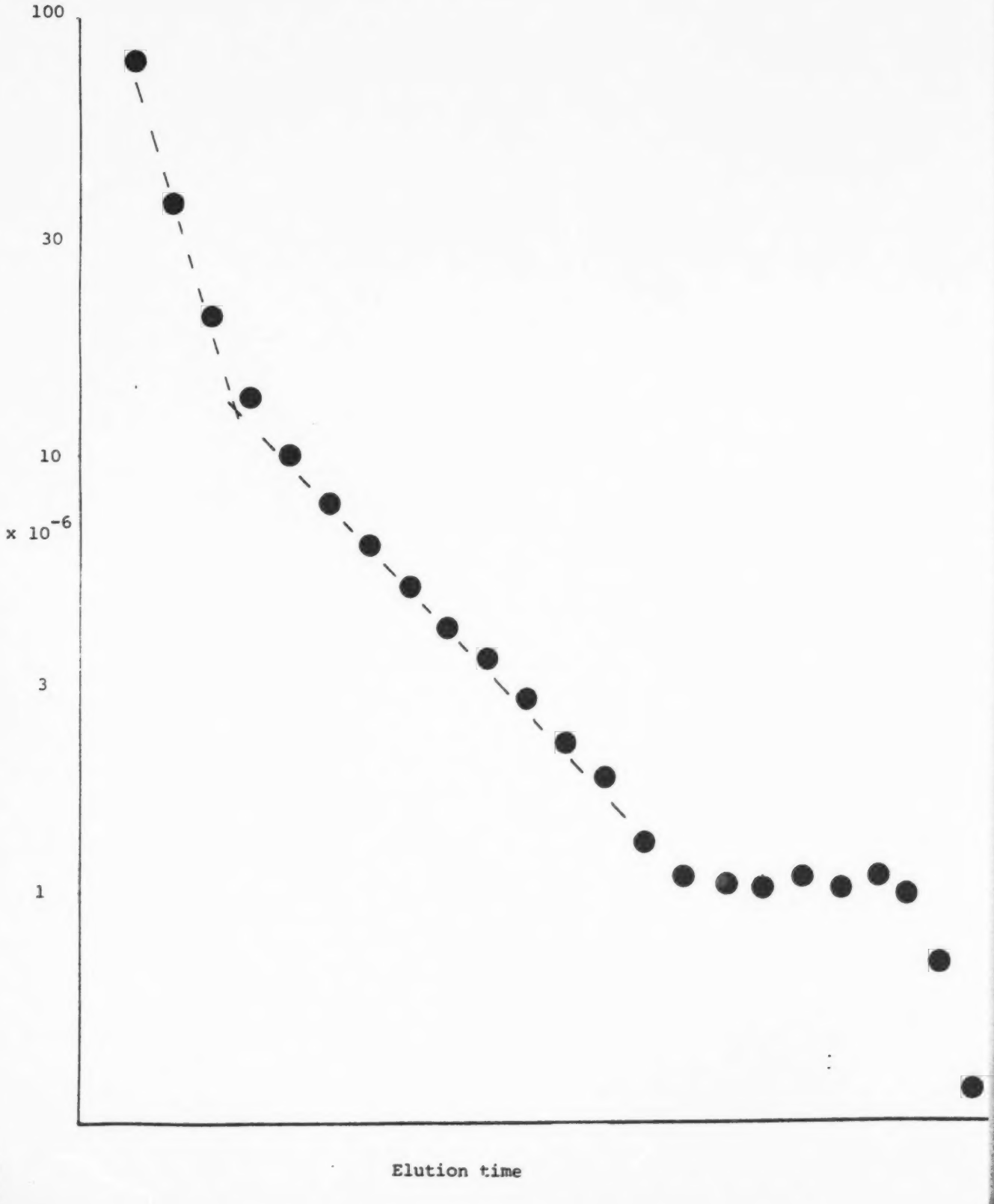


Figure 7: Reduction of degradation of Superfloc N-127 in solution containing 50 ppm ferrous salt and 200 ppm of certain stabilizers.

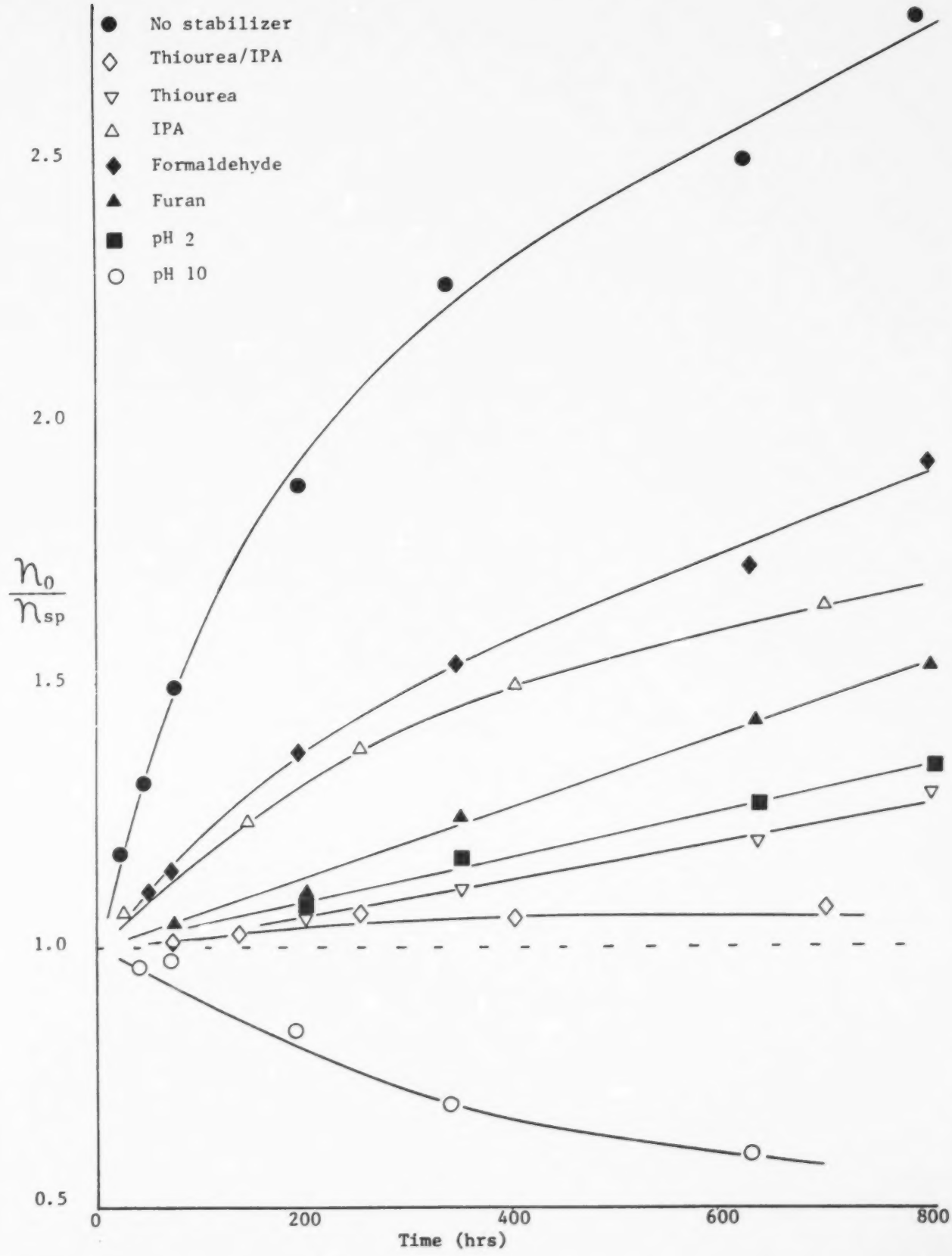


Figure 8: Increase of degradation of Superfloc N-127 in solution containing 50 ppm ferrous salt and 200 ppm of certain chemicals.

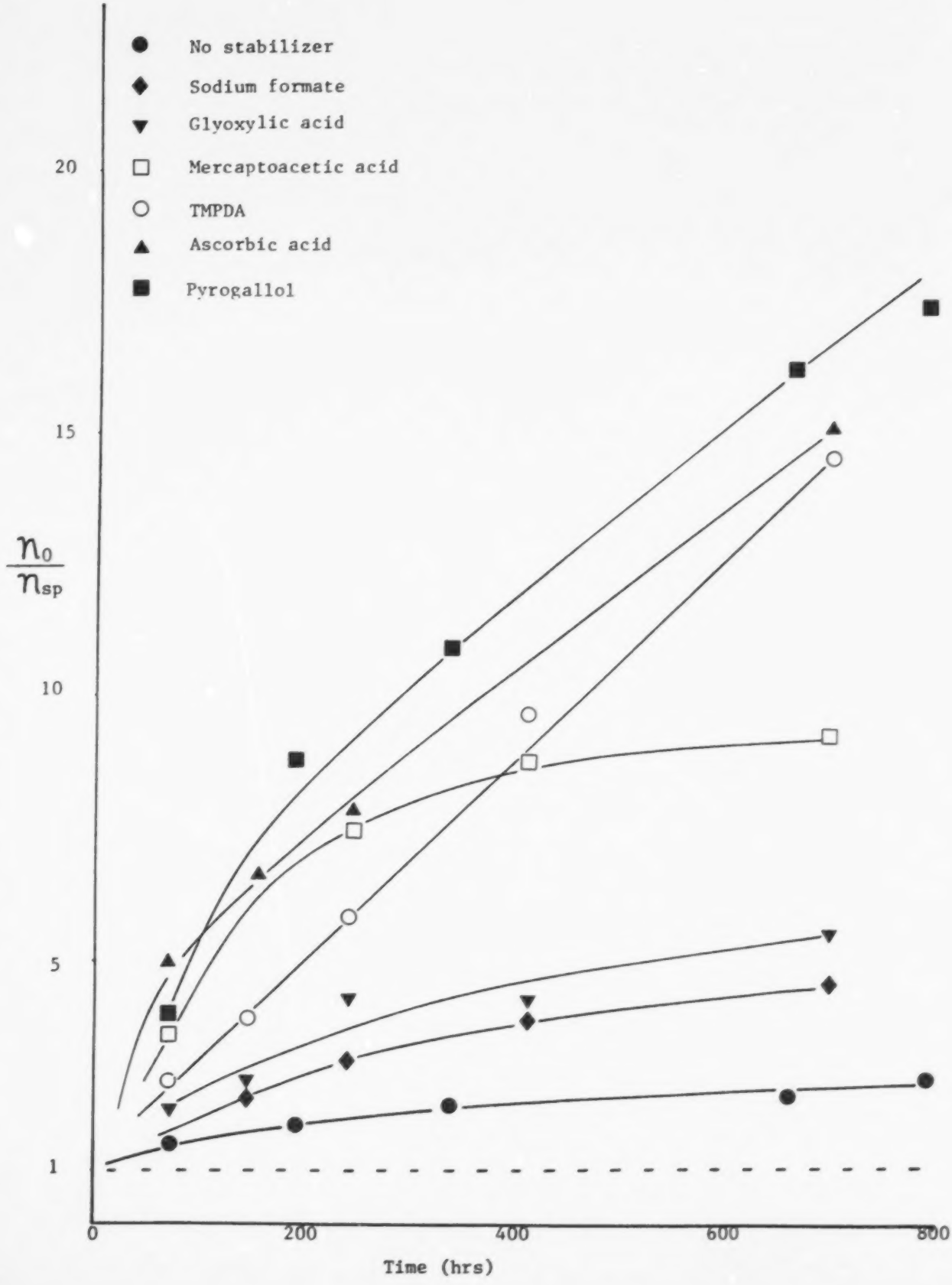


Figure 9 : Correlation of LALLS determined molecular weight with the normalized final viscosity of Superfloc N-127 after degradation.

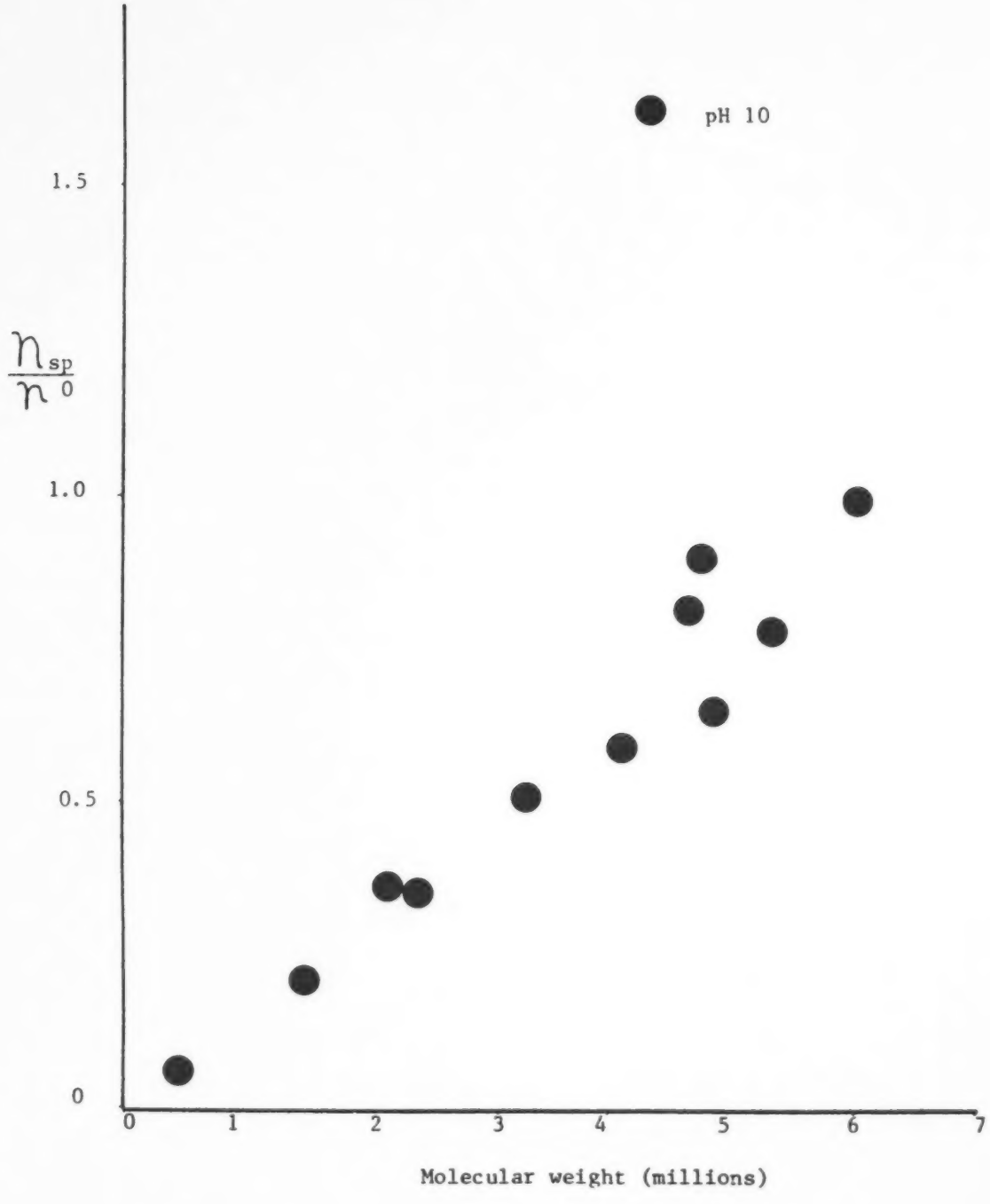


Figure 10: Variation of the inverse normalized specific viscosity of solutions of Perastol 2810 over time.

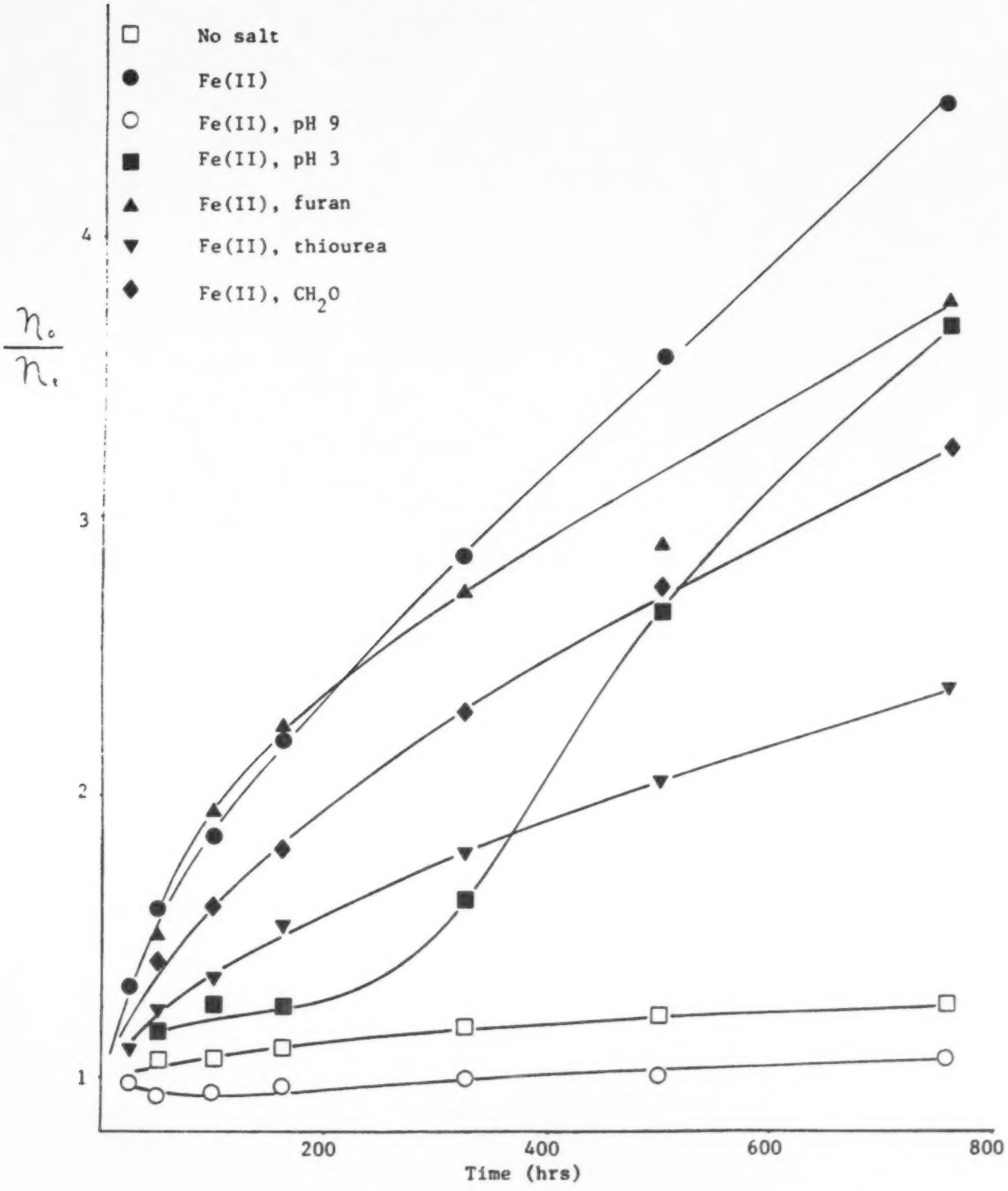


Figure 11 Variation of the inverse normalized specific viscosity of solutions of cationic polyacrylamide Calgon M515 over time.

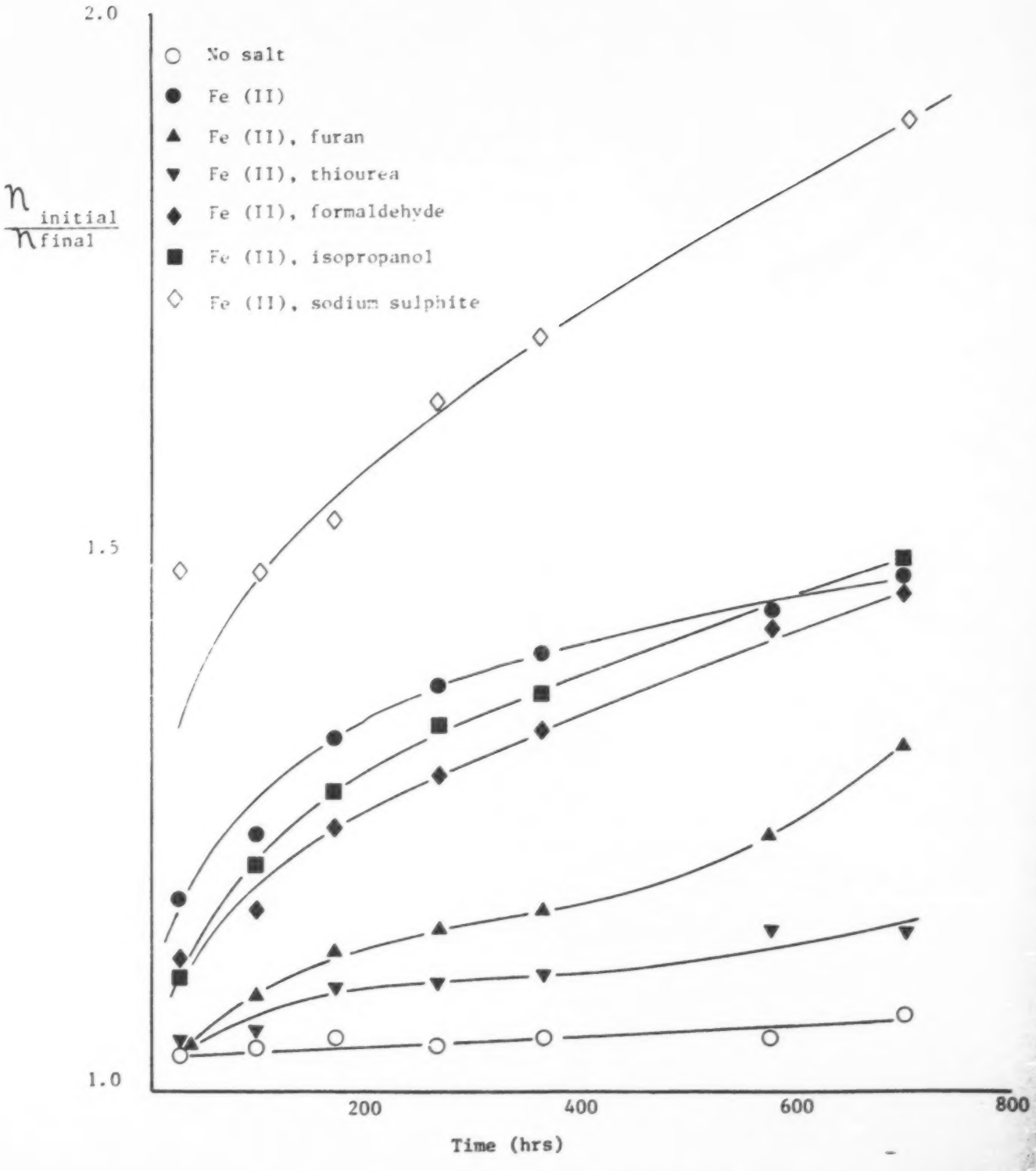


Figure 12 Comparison of the inverse of the final viscosity ratio, a measure of degradation, with the ionic nature of the polyacrylamide.

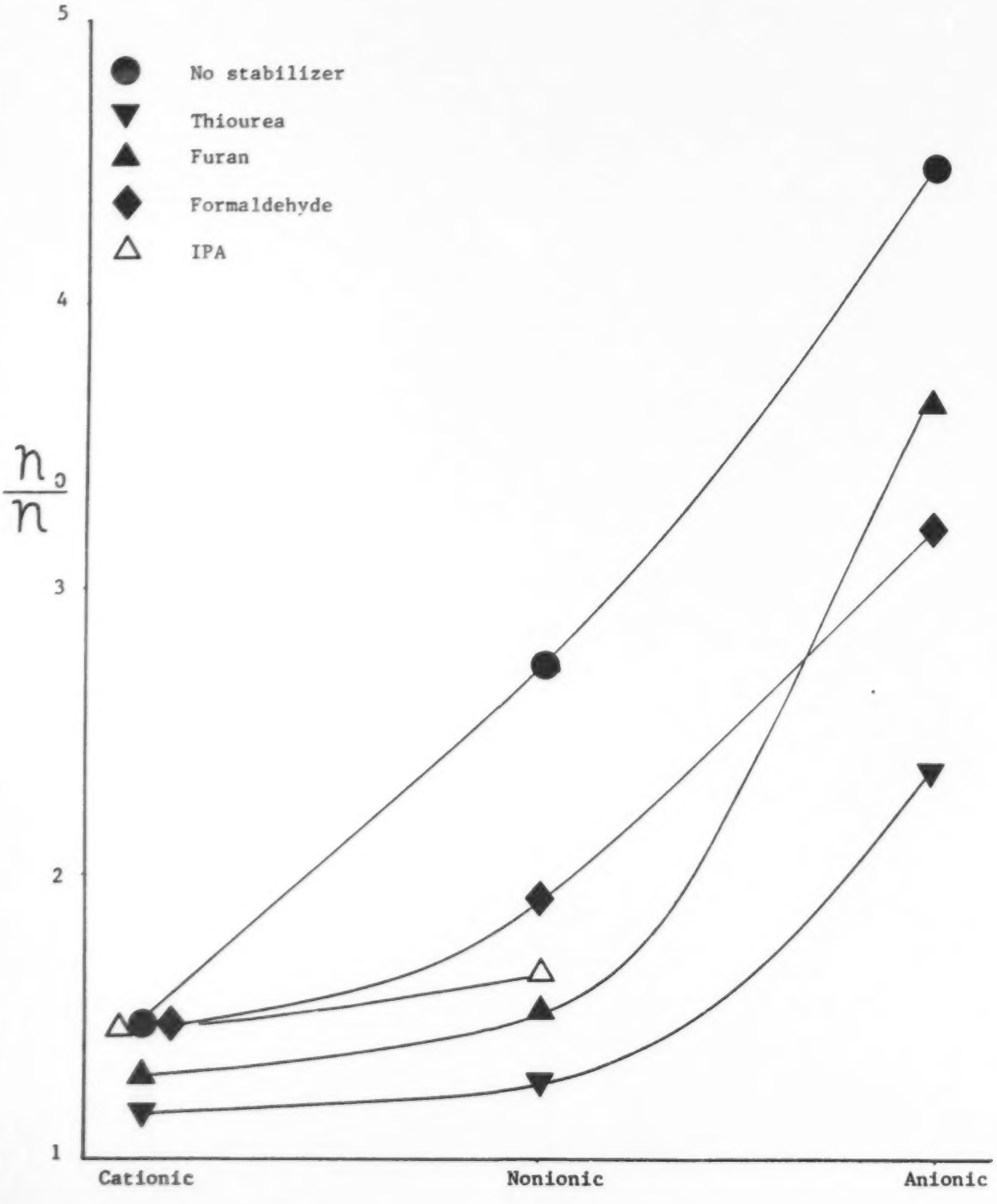
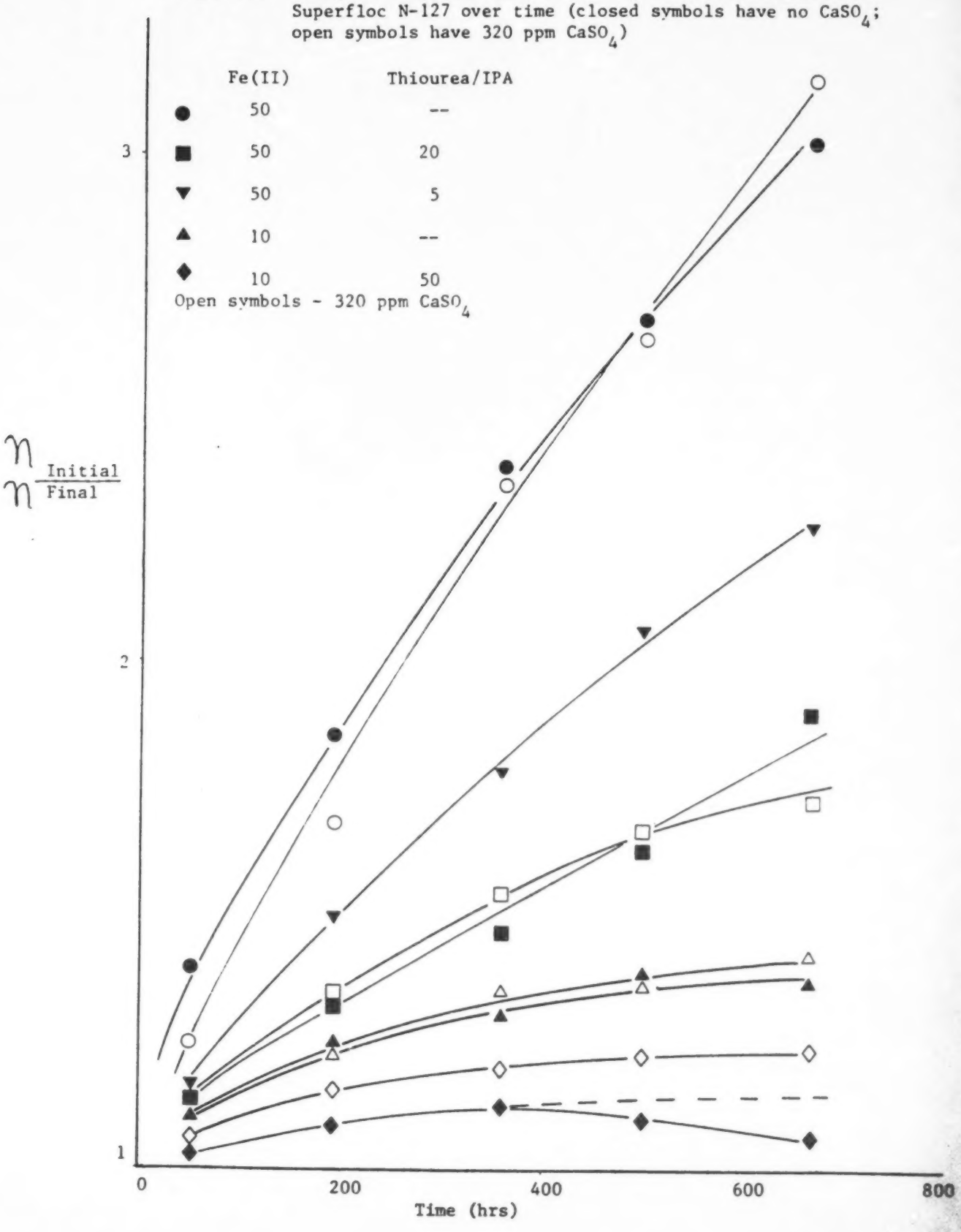


Figure 13 Change of initial/final viscosity ratio of solutions of Superfloc N-127 over time (closed symbols have no $CaSO_4$; open symbols have 320 ppm $CaSO_4$)



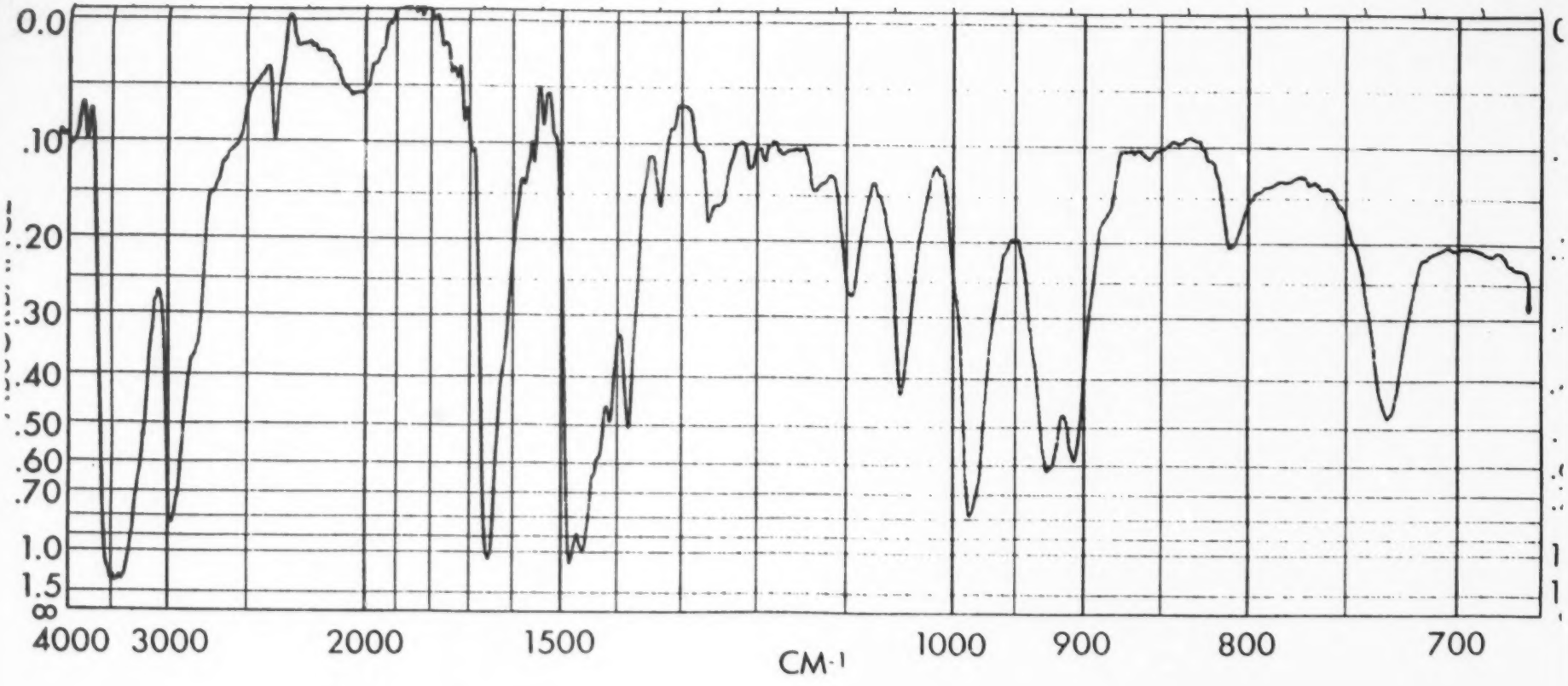


Figure 14 Infrared spectrum of 2,4-ionene (aqueous cast).

3400 cm^{-1}; water

2050 cm^{-1}; N-H

1480 cm^{-1}; $N-CH_3$

1100 cm^{-1}; C-N

970 cm^{-1}; CH_3-N

2950 cm^{-1}; C-H

1650 cm^{-1}; water

1460 - 1380 cm^{-1}; C-H

1050 cm^{-1}; C-N

730 cm^{-1}; $(CH_2)_4$

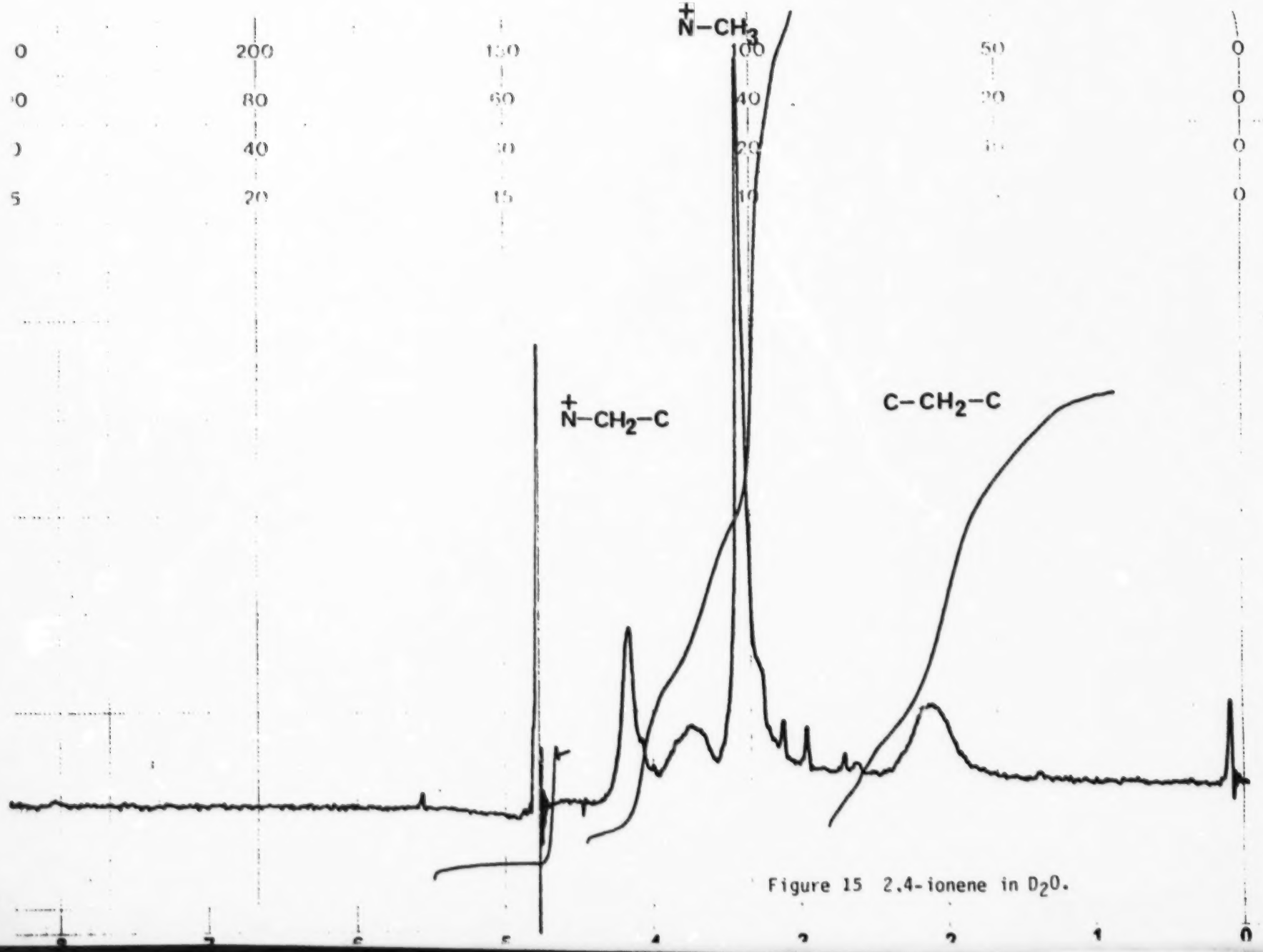


Figure 15 2.4-ionene in D_2O.

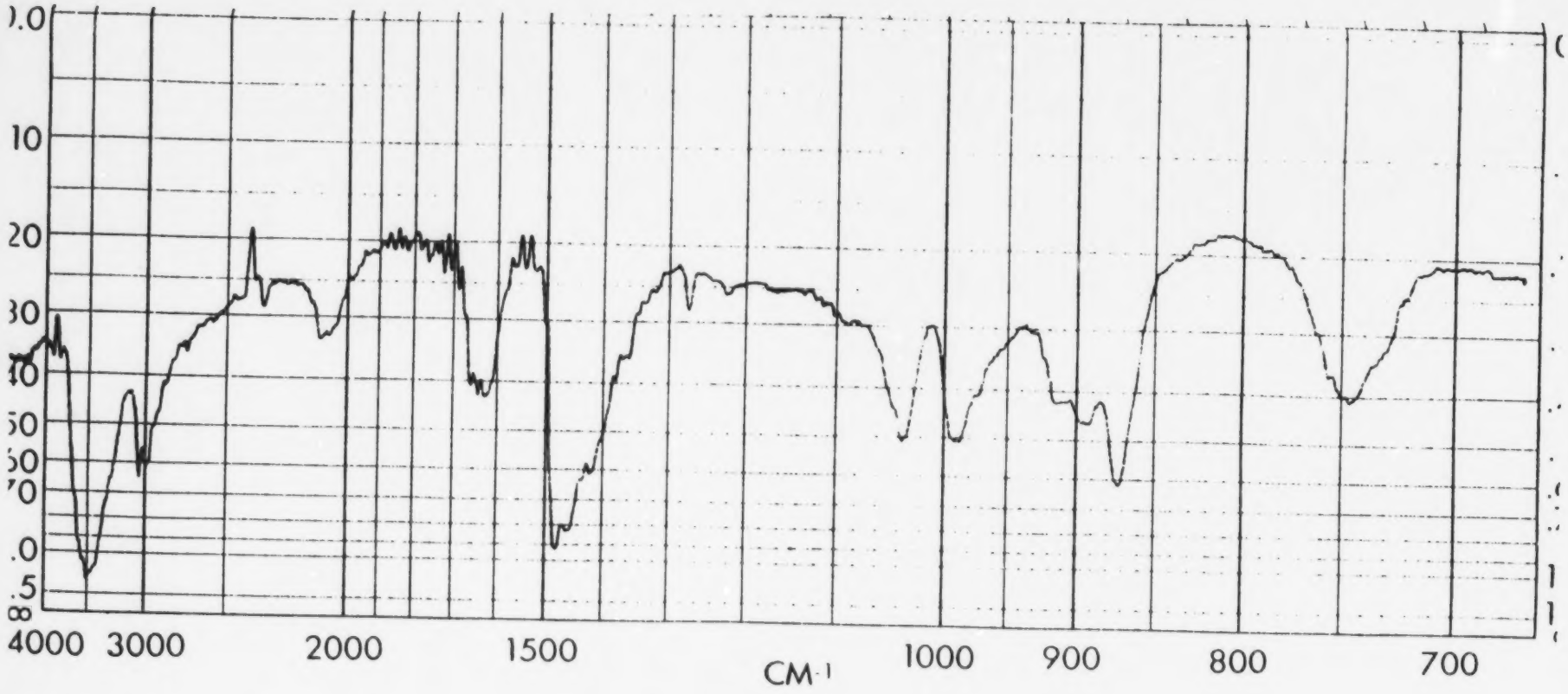


Figure 16 Infrared spectrum of 3,4-ionene (aqueous cast).

3500 cm^{-1}; water

2060 cm^{-1}; N-H

1480 cm^{-1}; $N-CH_3$

1040 cm^{-1}; C-N

3000 cm^{-1}; C-H

1640 cm^{-1}; water

1460 - 1380 cm^{-1}; C-H

980 cm^{-1}; CH_3-N

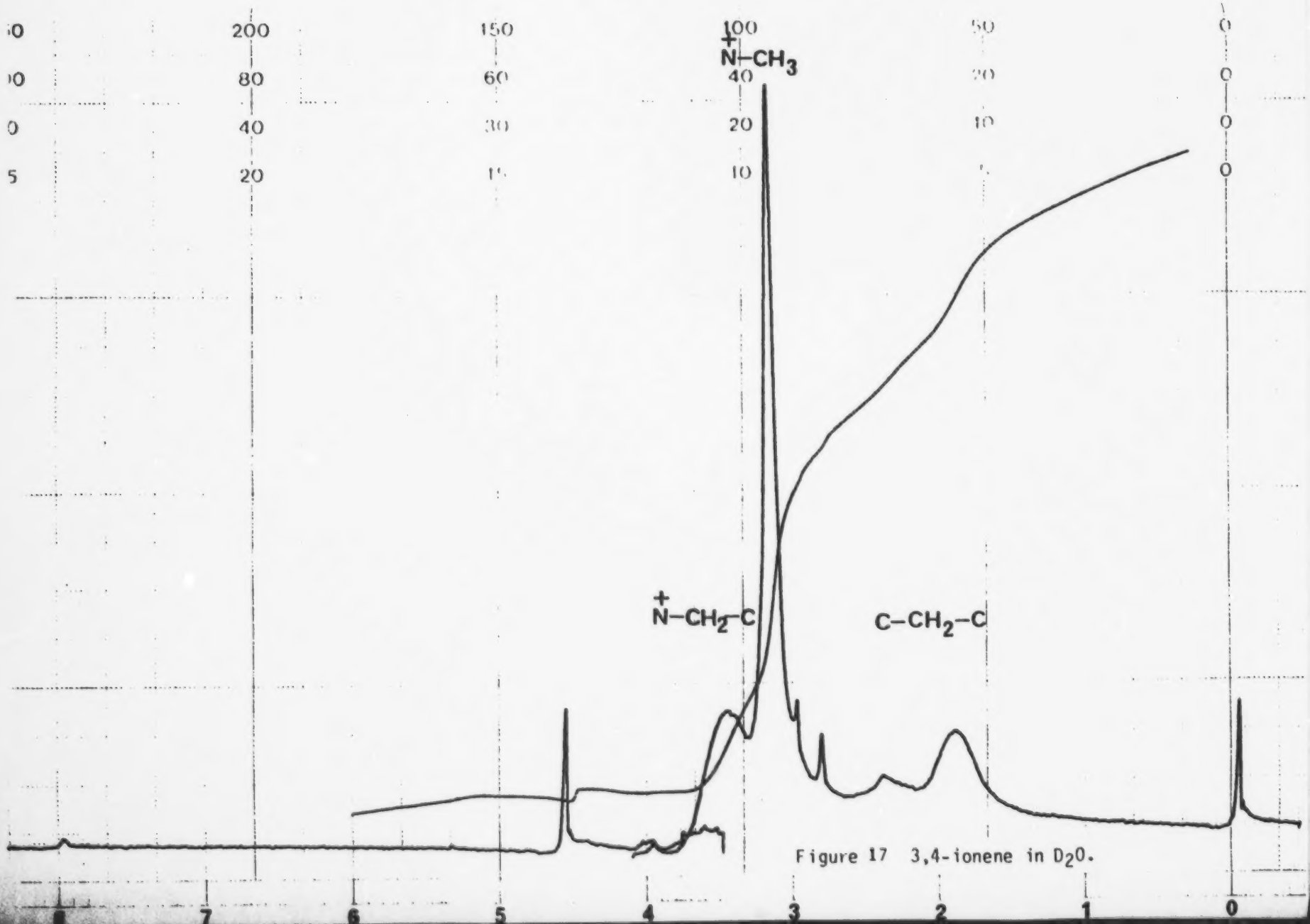


Figure 17 3,4-ionene in D_2O.

Figure 18 Decrease of the molecular weight of sample PS2806 over time upon ultrasonic irradiation at a setting of 40%.

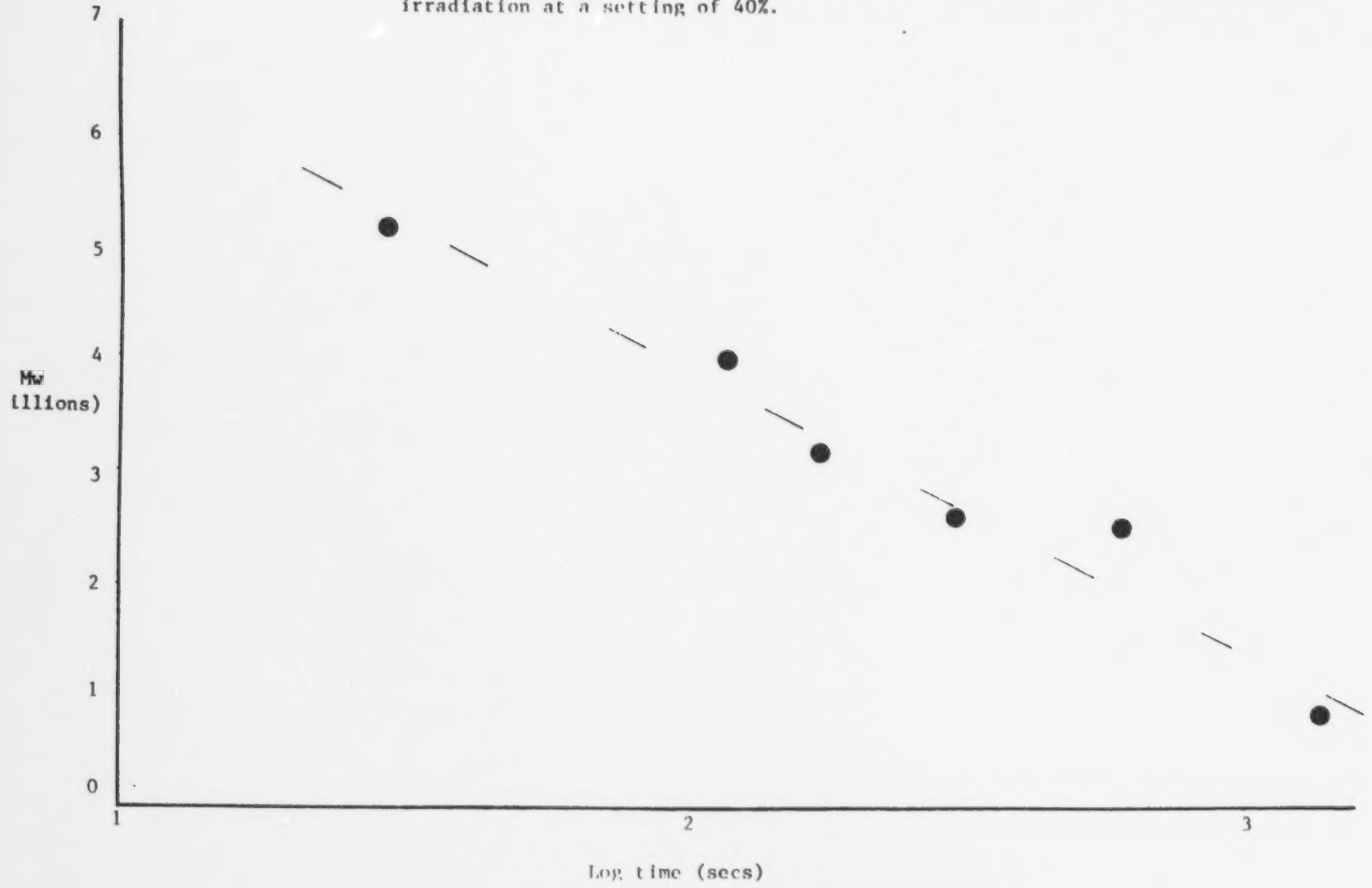


Figure 19 Decrease of the molecular weight of sample PS2806 over time upon ultrasonic irradiation at a setting of 80%.